TEXTILE RESEARCH

Publication of

United States Institute for Textile Research, Inc.

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Publication Office: Prince and Lemon Sts., Lancaster, Pa.

Editorial and General Offices: 65 Franklin St., Boston, Mass.

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Vol. V **January, 1935** **No. 3**

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Entered as second-class matter, November 17, 1932, at the Post Office at Lancaster, Pa., under the Act of Congress of March 3, 1879.

Issued monthly at Prince and Lemon Streets, Lancaster, Pa., for United States Institute for Textile Research, Inc., Boston, Mass.

Made in United States of America.

Subscription price $5.00 a year. Single copies .50.

The Editor's Page

THERE was brief reference in the December number to the plan for a scientific study of the warp sizing of cotton and synthetic yarns, to be conducted and financed co-operatively under the auspices of U. S. Instiute for Textile Research, Inc. The undertaking is the outcome of the largely attended conference on this subject, held in New York City last May, at which responsibility of promoting this research was laid on U. S. Institute's doorstep.

To Dec. 15th a little more than 25% of the $10,000 required to finance the project for two years had been subscribed or promised by manufacturers and allied firms, on the basis of $100 a year for the two years. While this was encouraging, in view of the fact that this co-operative financing of research was a new textile enterprise, it was realized that the balance of the financing might prove difficult and protracted.

At this juncture U. S. Institute was advised that the Directors of the Textile Foundation had acted favorably, at their meeting Dec. 10th, upon our prior invitation to consider the financing of this study, and had voted " to match any sum raised by the U. S. Institute, with the proviso that the Foundation's allocation of funds for this purpose be limited to $5,000."

Financing of the project can now be completed when 25 sponsors have been signed up at $100 a year for two years, but U. S. Institute would prefer that not less than 50 manufacturers would show their appreciation of the Foundation's co-operation, and also of research, by becoming sponsors at only $100 each.

They will do well to ponder the fact that if all textile research could be similarly financed co-operatively there would become available for this needed work more than $2,000,000, instead of the Foundation fund of something more than $1,000,000.

X-Ray Analysis of Textile Fibres

Part III.—Structure of the Cellulose Crystallite as Interpreted from X-ray Diffraction Data

By WAYNE A. SISSON[1]

Introduction

THE research program now in progress on the "X-ray Analysis of Textile Fibres" may be divided into three related parts:

A. Structure of the ultimate cellulose chain aggregate (crystallite or micelle).
B. Orientation of these aggregates in various textile fibres.
C. Relationship of structure and orientation to the physical and chemical behavior of the fibre.

Concerning the first part of this program (*i.e.*, the structure of the cellulose crystallite) there is a wide diversity of opinion among research workers. Staudinger [41, 42] has advanced the view that certain structural units, under the influence of normal covalence, line up regularly in one direction so that fibre molecules result. Meyer [26, 27] believes that the primary valence chains unite to form a bundle through reciprocal lateral attraction. The identification of cellulose crystallites with Nägeli's micellae, by Meyer and Mark,[28] and their explanation of the properties of cellulose on the basis of the micellar theory is well known. The micellar theory has been widely accepted as a working hypothesis for explaining the known facts about cellulose, but several investigators have doubted its necessity in order to explain the X-ray data,[2, 39] or the physical [30] and chemical properties [29] of cellulose fibres. It is conceded by these investigators that cellulose probably exists in the form of "micelles" in solution, or as regenerated cellulose, but they doubt the necessity of assuming the pre-existence of well defined micelles in natural fibres. However, all workers agree in the belief of the

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existence of some type of cellulose chain aggregate in natural fibres smaller than the fibre itself and larger than the cellulose unit cell deduced from X-ray analysis, and many methods have been employed by various workers to study the structure of the aggregate. These methods in general may be classified as either chemical or physical.

The chemical methods of total surface,[20] diffusion coefficients,[21] viscosity,[43] ultracentrifuge,[22] and methylation [17] are useful for estimating the average size of the cellulose "molecule" or "micelle" as it exists in colloidal solution, but due to the lack of knowledge concerning what happens during the solution process it is difficult to extrapolate the results to natural fibres. The microscopic and X-ray data are not limited in this respect, since the structure of the aggregate in natural fibres does not need to be altered during the examination. The difficulty here, however, lies in the fact that the reported dimensions of the micelle (400–1000 A.U. long and 40–60 A.U. in diameter) are intermediate between the range applicable to ordinary microscopic and X-ray methods, but by the use of special techniques the dimensions of the micelle in natural fibres have been estimated by the use of the Spierer lens,[44] diffraction by long wavelength X-rays [7, 8] and from the width of X-ray diffraction lines.[18]

Since many workers now believe that the micellar hypothesis is no longer necessary to explain the properties of cellulose, and since it has been recently shown that the Spierer lens is unreliable,[10] it is desirable at this time to make a critical examination of the X-ray data which have been of major importance for several years in supporting the micellar theory. The purpose of the present paper, therefore, is to enumerate the X-ray data; to discuss the various possible ways of interpreting the data; and to review briefly and to compare the existing theories for explaining the data.

Characteristics of Cellulose Diffraction Patterns

When a mass of random-arranged cotton linters is mounted in the usual manner [34] upon the X-ray diffraction apparatus in front of a flat photographic film and an exposure made, a typical Debye-Scherrer (powder) crystalline diffraction pattern, as shown in Fig. 1, is obtained. If the sample is a bundle of parallel ramie fibres, the same diffraction lines are obtained, but instead of the rings being continuous they now occur as short arcs, as shown in Fig. 2. The diffraction patterns shown in Figs. 1 and 2 may be described in terms of the following characteristics:

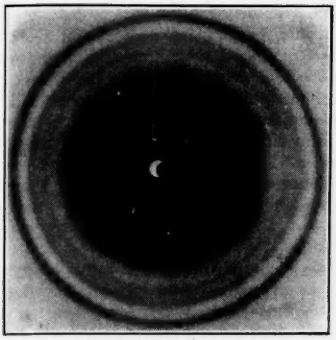

FIG. 1. Diffraction pattern of cellulose showing random orientation.

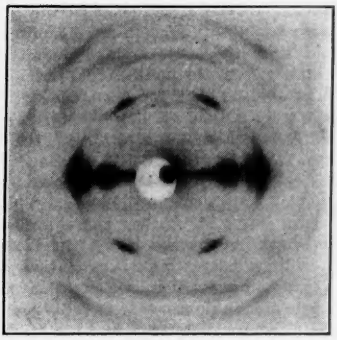

FIG. 2. Diffraction pattern of cellulose showing fibre structure.

A. Number of diffraction rings (monochromatic pinhole method).
B. Diameter of each ring.
C. Relative density of each ring.
D. Concentration of density into two or more ares around each ring.
E. Width or diffuseness of each ring.

Characteristics A, B and C appear to be constant for all cellulose materials. Characteristic D (and to a much less extent E) varies widely for different fibres; most fibres give a pattern intermediate between that shown in Fig. 1 and in Fig. 2.

Interpretations of Cellulose Diffraction Pattern

From each characteristic named it is possible to deduce certain information regarding the fine structure of cellulose fibres. The logical deductions from each characteristic will be discussed.

Number of Diffraction Rings

Since the X-ray pattern of cellulose is composed of definite diffraction rings we are forced to conclude that cellulose is crystalline in somewhat the same sense that sodium chloride is crystalline. If the cellulose chains were arranged in the form of a disorganized or amorphous mass, the X-ray pattern would consist of one or two broad bands instead of several diffraction rings.[5, 6, 12] The first major deduction, therefore, is that cellulose is crystalline.

From the fact that the diffraction rings are of a smooth uniform nature we make the second important deduction; namely, that the crystallinity of the fibre must be discontinuous. In other words, a single fibre is not a single crystal; it is a crystalline aggregate. This conclusion regarding the polycrystalline structure of a cellulose fibre is based upon the fact that a single crystal gives a Laue pattern composed of spots, and not uniform

rings.[6] However, if the single crystal is ground into smaller crystals, the Laue spots will become more numerous with progressive decrease in size; and since the spots from a definite crystallographic plane are a definite distance from the undiffracted beam on the film (monochromatic radiation), it is obvious that for a random-arranged sample the numerous spots will fall upon a Debye-Scherrer ring. These uniform Debye-Scherrer rings are obtained when the crystals of the diffracting sample become less than about 1×10^{-3} to 1×10^{-4} cm. in diameter.[6] It is certain, therefore, that the cellulose crystallites as they exist in natural fibres must be smaller than about 5×10^{-4} cm. in diameter. This is definitely proven by the fact that even a single fibre, when photographed by a micro method,[23, 24] gives smooth Debye-Scherrer rings instead of Laue spots.

Since microscopic examination shows many fibres to be built up of spirally wound fibrils, the question may be raised as to whether or not the fibrils are single crystals of cellulose. Calculations show, however, that they are probably too large to account for the type of diffraction pattern obtained from cellulose fibres. We are led to conclude, therefore, that even the fibrils consist of still smaller particles. In the present paper these small crystals of cellulose, which the X-ray pattern implies for natural fibres, will be referred to as "*crystallites.*"

Crystal Spacings

X-rays are not diffracted by individual atoms but by planes of atoms or molecules in the crystal structure, and the distance (d) between these crystallographic planes and the angle (θ) which the diffracted ray makes with the diffracting plane is related by the equation $n\lambda = 2d\sin\theta$. By the aid of this and other related equations and from our knowledge of the chemical structure of cellulose and the size and crystal habits of carbon, oxygen and hydrogen atoms, the arrangement of cellulose within the crystallite has been successfully deduced. This structure has been repeatedly described in the literature and will be only briefly referred to at this time. The detailed solution of the problem, involving some ten years of research by many workers may be found in the original papers previously reviewed in TEXTILE RESEARCH.[25]

In brief, the fundamental unit of cellulose structure is the ring-formed β-glucose residue, and these residues are connected by glucosidic oxygen bridges in the one-four positions to form long molecular primary valence chains in which the glucose rings are alternatively faced in opposite directions. These chains are arranged parallel to each other to form a unit cell with the dimensions $a = 8.35$ A.U., $b = 10.3$ A.U. and $c = 7.9$ A.U. This unit cell arrangement is extended or repeated in all directions to build up the crystallite.

With the exception of a few minor points this unit cell structure is now accepted by the majority of research workers and upon its basis all the spacings calculated from the X-ray diffraction pattern can be satisfactorily accounted for.

Relative Density of Diffraction Rings

The relative density of the X-ray diffraction rings can also be accounted for on the basis of the unit cell structure. The indexing of the planes, the positions and the densities of the lines have been computed by Andress[1] and are in agreement with experimental results.

We may feel fairly confident, therefore, that the number of X-ray diffraction lines, their corresponding spacings, and relative densities (*Characteristics A, B, and C*) may be satisfactorily explained by the unit cell structure. These three characteristics of the pattern appear to be identical for all native cellulose, regardless of its source,[32] and this indicates that the crystalline structure of cellulose is the same for all natural cellulose fibres. As to the arrangement of the cellulose crystals in the fibre walls, however, there is a wide variation among different fibres and sometimes in the same fibre.

Localized Intensity Around Diffraction Rings

The density distribution around the diffraction ring is directly related to the orientation or arrangement of the cellulose crystallites within the fibre.[38] If a bundle of parallel fibres arranged perpendicular to the X-ray beam gives uniform rings, such as shown in Fig. 1, the crystallites have a random arrangement with reference to the fibre axis. If the lines are concentrated into localized intensity maxima, such as shown in Fig. 2, the crystallites have a common axis oriented with reference to the fibre axis. The type of pattern shown in Fig. 2 is called a "fibre pattern," and is similar to that obtained by rotating a single crystal around one of its axes (rotation pattern). Examples ranging from an almost perfect fibre pattern to a completely random oriented pattern may be found among natural fibres, and in each case the density distribution around the X-ray diffraction rings can be satisfactorily accounted for by the crystallite orientation within the fibre.[37]

Width of Diffraction Rings

In well-oriented cellulose fibre patterns (Fig. 2) where the crystallites have their *b* axes parallel to the fibre axis, the width of the lines arising from the planes parallel to the *b* axes (equator line) is greater than the width of the lines arising from the planes perpendicular to the *b* axes (meridian line). There are several possible ways of explaining this difference in line breadth: it may be due to particle size, strain, impurities, imperfectly formed crystals, or to a combination of any of these. Each of these possibilities will be discussed briefly.

Particle Size: The difference in line breadth in the direction of the meridian and the equator may be very satisfactorily explained by assuming the existence of long rod-like submicroscopic crystallites. The interpretation is based upon the fact that when the average particle size becomes less than about 1×10^{-6} cm., the diffraction lines become broader and more diffuse due to the lack of sufficient diffracting planes.[6] Thus, if a crystallite with a length (direction of *b* axis) greater than 1×10^{-6} cm. and a width (direction of *a* and *c* axes) less than 1×10^{-6} cm. is assumed, the planes normal to the *b* axis would give a diffraction line of average breadth, while those parallel to the *b* axis would give a broader line. This is the usual explanation given and, as will be pointed out later, it is possible to estimate the dimensions of the crystallite from the width of the diffraction line.

Strain: It is well known that a condition of strain within a crystal will produce a broadening of the diffraction lines, and a critical review of the subject has been recently published by Barrett.[4] Herzog [19] has advanced

the theory that tension during growth causes the orientation present in natural fibres. Farr and Eckerson [14] have observed that when cotton fibres are treated with solvents of the non-cellulose cementing substances, the fibrils which have been in the form of a spiral immediately straighten out. This would indicate that the fibrils have been deposited in a state of tension during growth. Since the action of either strong acids or bases and certain other swelling agents will modify the crystalline structure of cellulose (mercerized structure) and since a reversion of this structure is very difficult, it has been assumed that native cellulose is deposited in an unstable form in growing fibres.[28] It would seem equally logical to assume that similar forces operating during growth may produce an internal strain within the crystal, and this strain, if present, would tend to increase the line breadth. Furthermore, since considerable lateral shrinkage occurs when a fibre dries, it is possible that this shrinkage may produce a slight bending or distortion of the planes parallel to the fibre axis.

Impurities: That a small amount of foreign atoms included in the crystal lattice will produce a broadening of the diffraction lines has been clearly demonstrated in the case of metals.[12] Since many non-cellulose materials are so closely associated with cellulose during its formation in the cell wall, it is possible that small amounts of these materials may become included in the cellulose crystals and produce a distorted lattice. It is even possible that the material between the crystallites may have its own diffraction pattern which is superimposed upon the cellulose pattern and alters its appearance. Examination of a large variety of fibres reveals the fact that fibres of the bast or woody type almost always have broader equator lines than cotton. This appears to be easily explained on the assumption that the diameter of the micelles varies in different fibres, but it has been observed that if the cellulose is isolated from the non-cellulose materials, the resulting cellulose gives an X-ray powder-pattern which approaches that of cotton cellulose in the sharpness of its diffraction rings. It is difficult to picture this change as being due to an increase in micellar size during the removal of the non-cellulose materials. It would seem more logical to assume that the diffuse lines of the original cellulose fibres are due to the presence of non-cellulose materials or to strain. If the broadening of the diffraction lines is due to either impurities or to strain, the question may arise as to why the equator and the meridian lines are not equally effected. It will be remembered in this connection that the substitution of the hydroxyl groups for other groups often effects only the planes parallel to the cellulose chains, the identity period remaining constant.[25]

Imperfect Crystals: The limiting resolving power of a crystal is influenced by the arrangement of the atoms or molecules which occupy the points in the space lattice, and for that reason the breadth of a diffraction line cannot be made infinitely narrow. Since whole glucose residues ($C_6H_{10}O_5$) occupy the points of the lattice, the diffracting planes through the corresponding rows of cellulose chains cannot be as nicely arranged as those of many other crystals. These imperfect planes parallel to the *b* axis may possibly account, at least in part, for the width of the equator lines. Furthermore, as evidenced from an examination of a three dimensional model, the sharper vertical lines in the fibre pattern seem to be in accord with the more perfect arrangement of the atoms forming the planes normal to the cellulose chains. It is also possible that the concept of imperfect

crystals, as postulated by Zwicky for the more familiar crystals,[46, 47] may apply equally well to cellulose and thus account for the imperfections of cellulose crystallinity.

From this discussion it is obvious that in order to definitely attribute the line-breadth of cellulose to any one factor, one must be sure that the other possibilities are absent. For many well-known inorganic crystals it is possible to make this assumption, but when dealing with the complicated less-familiar structure of cellulose the possibility of one or more of these factors influencing the line-breadth cannot be overlooked. Upon examining the X-ray photograph of a material which gives broad diffuse lines it is impossible to say whether the broad lines are due to crystal size, impure crystals or distorted crystals, unless some of the possibilities can be eliminated with the aid of additional evidence. In the case of cellulose where such additional information is lacking, it would seem just as reasonable to assume that the broad lines are due to an imperfect crystalline structure as to assume that they are due to the presence of micelles having a definite crystal size.

Interpretations of Soft Radiation Data

Instead of using the indirect line-breadth method employed by Hengstenberg and Mark,[18] Clark and Corrigan[7, 8] used soft X-rays ($K\alpha = 9.86$ A.U. for magnesium radiation) to measure directly the dimensions of the micelle. The method is based upon the assumption that if well defined micelles are present in cellulose then they should diffract long wave-length X-rays just as the glucose residues diffract shorter wave-lengths ($K\alpha = 1.54$ A.U. for copper radiation). Several diffraction lines obtained by this method have been offered as additional support for the micellar hypothesis.[7, 8, 11]

It was thought of interest by the author to further investigate the possibilities of the method for studying the fine structure of various cellulose materials. For this investigation a hot filament X-ray tube and vacuum camera were used.[11] In order to check and calibrate the apparatus a sample of stearic acid was oriented on a smooth lead surface[45] and the perfectness of the orientation and the spacings corresponding to the chain length determined by copper radiation. The average spacing obtained by copper radiation was 48.2 A.U. With magnesium radiation the same sample gave an average value of 47.4 A.U. Repeated efforts, however, to obtain characteristic diffraction patterns from thin specimens of ramie, cotton and *Valonia* were unsuccessful. Although several lines were obtained from these materials it was difficult to interpret or repeat the data.

If micelles give a diffraction pattern one would expect a fibre pattern to be obtained from the well-oriented ramie fibres; however, only continuous rings were obtained, and it may be possible that these rings are due to some other effect, such as electron diffraction. In view of our knowledge concerning the behavior of other colloidal materials towards copper radiation, it does not seem logical to expect sharp diffraction lines to be obtained from colloidal particles. Rather would one expect broad halos corresponding to the closest approach of the micelles to each other, since it is not likely that the regularity of the micelles in the fibre should approach that of atoms or molecules in a crystal lattice. Furthermore, the existence of well-defined micelles in natural fibres does not seem to be the only pos-

sible interpretation of soft radiation diffraction data. The concept of a continuous structure with large spacings, which will be discussed later, may offer an equally logical explanation, just as it may explain the crystalline discontinuity of cellulose implied in the usual diffraction pattern.

Interpretations of Other X-ray Data

In the previous two sections our attention was devoted to the possible interpretations of the X-ray diagram of a bundle of cellulose fibres. Aside from the characteristics of the diffraction patterns themselves, important information regarding the fine structure of cellulose may be obtained also by observing how these characteristics are effected by various physical and chemical processes. Several of the most important processes which give information in this connection will be discussed.

Swelling: In certain kinds of swelling, designated as intermicellar, the X-ray diagram is not affected by the swelling process.[23] If the swelling was due to a change in the volume of the crystallite there should be a corresponding shift in the diffraction spacings. Since there is no change in the X-ray pattern we are forced to conclude that cellulose must consist of definite crystallites held together by a non-crystalline material, and that it is this amorphous material which is changed by the swelling process, the crystalline portion remaining uneffected. In other cases, such as the action of sodium hydroxide, the crystal structure may be changed; yet, even here, the crystallite appears to remain intact as evidenced by extending the fibre.

Deformation: If a stress is applied to a swollen fibre a certain amount of viscous flow takes place. The only effect produced upon the X-ray diagram by a process of extension is a change in the intensity distribution around the diffraction ring, corresponding to a change in the orientation of the crystalline material.[24, 36] If the crystalline structure was disrupted by the deformation, as is the case with metals, it should be detected by a change in the diffraction pattern, but since there is no change it is inferred that the crystallites move as a unit during the flow (micellar flow).

Solution: When native cellulose fibres are dispersed and the cellulose later regenerated as rayon fibres, we again obtain a definite crystalline X-ray pattern (mercerized). Furthermore, when the fibre is extended there is also the unmistakable evidence of cellulose chain aggregates which move as a unit by slipping over each other. This would seem to indicate that particles of crystalline cellulose remain intact during the solution and precipitation process; however, individual chains may also exist in solution[33] and it is possible that there may be a certain amount of recrystallization during the regeneration of the cellulose.

Degradation: In Part II[34] a preliminary report was given of an X-ray study of fibre decomposition and oxidation. These studies show that the main bulk of the crystallized part of the cellulose is changed only after the original physical properties of the fibre are practically destroyed. This would seem to indicate that the main portion of the cellulose exists in the form of crystallites which are less subject to attack than the intercrystalline material or forces which bind them together. When the crystallites are finally attacked the degradation appears to take place first on the surface.

In addition, many other processes which indicate a discontinuity of the crystalline structure could be cited, but none of these offer irrefutable

arguments for the pre-existence of well defined micelles in native fibres. As pointed out by Astbury,[2] in each case the argument for their pre-existence rests upon acts of disruption and are therefore open to suspicion. The data definitely points to the existence of cellulose chain-aggregates or "micelles" in the altered fibre, but as to the exact nature of the crystalline discontinuity in the original native fibre no definite conclusions can be drawn from this type of data.

Theories of Cellulose Structure

The X-ray evidence discussed in the previous sections imply: (1) that cellulose must be crystalline; (2) the crystals must be small; (3) they must be arranged with a common crystalographic direction parallel to the fibril axis; (4) they must move as a unit during swelling and deformation; and (5) they must possess some characteristic structure which causes the breadth of the equator lines to be greater than the meridian lines. As to the exact nature of the crystallite implied by the X-ray data there is, however, no universal agreement. Any theory of the structural unit between the visible fibre and the cellulose chain must satisfy, in addition to the X-ray data, other data from many sources. In the present paper no attempt will be made to enumerate and evaluate all of these or to discuss all of the possible ways of explaining the data. The subject matter will be confined to a description of the three theories which appear to offer the most plausible explanation of the most important facts about cellulose, particularly the X-ray data. These theories will be designated as the micellar theory, the continuous structure theory, and the cellulose particle theory.

Micellar Theory: As outlined earlier in this paper, the X-ray data seem to be satisfactorily explained on the assumption that cellulose fibres are built up of crystalline cellulose chain-aggregates which are submicroscopic in size, are much longer than they are thick, and are arranged with their long axes roughly parallel or spiral with respect to the fibre axis. In the absence of any other known structural unit below the fibril, these cellulose chain-aggregates have been commonly associated with Nageli's micellae. As postulated by Meyer and Mark,[28] the fibre wall is built from these micelles in very much the same manner as a solid wall composed of bricks. Primary valence forces hold the glucose residues in the form of a chain; secondary valence forces hold the chains alongside each other in a micelle; and tertiary forces, or amorphous cementing material between the micelles, hold them together. The micelles are formed in nature by being built up from cellulose chains to a definite size, characteristic of the specimen, and then deposited in the cell wall.

When the fibre is treated with a swelling agent the sorption of the liquid and the swelling in many cases take place between or on the surface of the micelle (intermicellar) and the crystalline structure is not affected. If the fibre is subjected to stress while in the swollen condition the micelles rotate or move as a unit. For example, a straight tension will rotate the long axes of the micelles parallel to the axis of tension. When a fibre is ruptured the break does not occur through the micelles, with a severing of the cellulose chains, but by slipping of the micelles over each other. When a native fibre is dispersed the solvating process begins with a swelling and a subsequent

dissolving of the intermicellar material, and if the conditions are right the micelles are dispersed without essentially altering their size. By further action of the reagent the micelles can be broken into fragments and eventually may be split into singular chains. Thus, one of the main difficulties in determining the size of the micelles in solution is in knowing just where the solvating process has stopped.

Hengstenberg and Mark [18] have estimated the size of the micelle in ramie to be approximately 50 A.U. in diameter and over 500 A.U. long. Their calculations are based upon a theoretical relationship between particle size and the breadth of the diffraction line at half maximum intensity. The method has been employed with success to estimate the particle size of many materials within the colloidal range of 1×10^{-6} cm. to 1×10^{-8} cm., but as pointed out by Meyer and Mark [18] the method is only valid provided the following assumptions can be made:

1. Absorption of X-rays by the sample is negligible.
2. Micelles have only one definite size.
3. All micelles have identical crystal structure.
4. Heat motion has no appreciable effect.
5. The lattice structure of each micelle is perfectly formed (*i.e.* not deformed by the presence of impurities or strain).

As discussed previously, these assumptions may be made for many familiar crystals, but in view of the complicated structure of cellulose there may be some question regarding the assumptions when applied to cellulose.

Although the micellar hypothesis is not the only way to explain the X-ray data, it is perhaps the most widely accepted, and for several years the X-ray has championed the micellar hypothesis. Among some research workers, however, there is a growing belief that the micellar hypothesis is not necessary in order to explain the known facts about cellulose, and as a substitute they have suggested what will be referred to as the "continuous structure theory."

Continuous-Structure Theory: Although the X-ray data implies a discontinuous crystalline structure of cellulose, there is, however, as just pointed out, no definite proof that the discontinuity consists of discrete crystalline particles or micelles as postulated by the micellar theory. In explaining the X-ray data it is also possible to assume a more or less continuous structure in which the crystalline regularity of the cellulose chains may be interrupted by minute warped or faulty sections. The chains need not be broken lengthwise or separated sidewise to form individual crystals in order to explain the X-ray data; these faulty or irregular crystalline regions would produce in the X-ray diagram the same effect as though they were amorphous material separating well defined crystallites.

In the young fibre the cellulose is deposited layer upon layer in the cell wall. Certain regions of these layers will possess a definite crystalline regularity of cellulose chains and these regions may be considered as "crystallites"; in other regions the chains will have an irregular arrangement and these may be considered as "amorphous" or "intercrystalline" cellulose material. When the fibre is swollen or dispersed the liquid enters the mesh-work of regular and irregular regions and separates the material into minute particles of cellulose. These particles, as they behave toward the X-rays and as they behave toward swelling and deformation, or as they

exist in solution and in a regenerated state, may be considered as "micelles."

Peirce [30, 31] has suggested that "there is no reason to suppose pre-existent boundries in the cell wall; . . . It is more in conformity with the evidence to suppose that the molecular order only approximates to crystalline perfection, being interspersed with partial local discontinuities, which have the effect on diffraction as have the continuous boundries of crystallites." Neale [29] finds no necessity for assuming the existence of well-defined micelles in order to explain the chemical behavior of cotton fibres, and as an alternative explanation for the X-ray data has suggested the possibility of a "rhythmic variation from a perfectly crystalline structure without sharp discontinuities." Sponsler [39] has suggested that the chains may not be broken to form separate particles, but that their regularity is interrupted by minute warped or bent sections of these long chains, which cause these regions to behave essentially amorphous to X-rays. This explanation is more in keeping with the general mechanism of cell-wall growth (deposition of individual chains layer upon layer in the cell wall) as advocated by Sponsler.[39, 40] Astbury [2] has pointed out the possible analogy between the micellar structure of wool fibres and the secondary structure or co-existence of perfection and imperfection in the more familiar crystals, as postulated by Zwicky. Astbury has suggested that instead of the pre-existence of sharply defined micelles, "rather does the available evidence point to a self-contained system riddled through and through by crystallization 'faults.'"

A continuous structure in natural fibres, as contrasted to a "micellar structure" in regenerated cellulose, appears to explain certain fundamental differences in the tensile and plastic behavior of natural fibres and of rayons. In cotton the tensile strength is high and increases with increasing moisture; in rayons it is low and decreases with increasing moisture.[5, 30] Also the extension-load ratio decreases with increasing load for cotton and increases for rayons. These differences may be explained by assuming that molecular chains themselves are broken when a cotton fibre is ruptured. Moisture would tend to loosen the lateral adhesion between the chains and tend to equalize the stress distribution, thus increasing the strength and decreasing the extension-load ratio. In regenerated cellulose, on the other hand, the mechanism expected of a micellar structure appears to hold. Increasing moisture weakens the cohesion between the cellulose chain-aggregates ("micelles") and hence lowers the tensile strength and increases the extension-load ratio, due to the viscous flow of the aggregates.

As just pointed out, the continuous-structure theory probably explains the physical and chemical properties of natural fibres better than the micellar theory, but, on the other hand, the micellar theory appears to better explain the X-ray data. The continuous-structure theory would explain the Debye-Scherrer diffraction rings on the basis of a mesh-work of perfect and imperfect crystalline cellulose; it would explain the width of the diffraction rings as being due to the size of the perfect crystalline sections or to the presence of the imperfect crystalline material, but the explanation of both of these characteristics of the X-ray diagram is more complicated than that offered by the micellar hypothesis. It is also more difficult to account for the various types of orientation (spiral structures) found among natural fibres on the basis of a continuous structure. However, experience has taught us that the conception of crystalline cellulose cannot be reduced to

the simplicity of sodium chloride, and perhaps the more difficult explanation is the more logical one.

Cellulose-Particle Theory: The recent description of the formation of cellulose membranes by microscopic particles of uniform size in linear arrangement by Farr and Eckerson [14] has led to the suggestion by Farr and Sisson [15] that it might be possible to substitute the cellulose particle for the micelle in the current interpretation of X-ray diffraction data. These particles are ellipsoid in shape; are arranged with their their long axis parallel to the fibril axis; exhibit all the properties of crystalline cellulose; and are covered with a thin coating of pectic material. They may be observed in the cytoplasm of young fibres, and during the growth of the fibre they unite end to end to form long bead-like strands which are deposited in the cell wall. Further confirmation of their identity has come from a separation of the mature cell membranes into fibrils and these, in turn, into particles by means of suitable pectic solvents.[15]

It has been shown that the arrangement of these particles in the cell membrane completely explains the optical [14] and X-ray data [16] of the fibre. The size of the particles are well within the limit necessary to give the Debye-Scherrer patterns characteristic of cellulose, and, since the cellulose chains are arranged parallel to the long axis of the particle, the conception of particles arranged end to end to build up the fibril would completely account for the X-ray fibre patterns of well-oriented cellulose fibres. There is only one characteristic of the X-ray diffraction pattern which is not obviously explained by this new conception of cellulose membranes; namely, the width of the diffraction lines. However, it has been suggested [16] that this characteristic may be explained by assuming the crystal structure of the particle to be sufficiently imperfect to account for the breadth of the X-ray line.

The other X-ray data can also be accounted for on the basis of the particle theory. Intermicellar swelling may be pictured as taking place in the cementing pectic material without effecting the crystallinity of the particle. Plastic flow could take place by the particles sliding over each other. Solution would consist of the particles first being dispersed, followed by a penetration of the liquid into the imperfect crystalline regions which would produce a splitting of the original particle into fragments and finally into individual chains, or perhaps fragments of the original chains which extended the entire length of the particle. Other processes which change the physical properties, but not the crystalline structure, may be assumed to affect only the cementing pectic material.

The cellulose-particle theory also appears to offer an explanation of the difference in physical strength between natural fibres and rayons. The increased tensile strength and the decrease in extension-load ratio with moisture increase of cotton may be explained by assuming that the moisture lossens the lateral adhesion of the fibrils and thus equalizes the stress distribution among them. Microscopic observation indicates that the fibrils do have less lateral cohesion than the particles do end-to-end cohesion since the fibre is separated first into fibrils and later into particles when treated with suitable dispersing agents. Furthermore, it would seem more reasonable to assume that the moisture lessens the rigidity of the non-cellulose cementing material between the fibrils, rather than to assume that the secondary valence forces between the chains are loosened, as is necessary to assume for a continuous structure.

Comparison of Theories

The micellar theory explains very satisfactorily the X-ray data. Its weakness lies in its inability to explain the difference between the physical and chemical behavior of natural fibres and of rayons, and also other chemical properties and observations about natural fibres. The continuous-structure theory is designed to meet these shortcomings of the micellar theory, and in turn its weakness is its inability to account for all the X-ray data in a simple manner. The cellulose-particle theory includes, to a certain extent, the essential features of both the micellar and the continuous structure theory.

The essential attribute of the micellar theory is the existence of discrete rod-like submicroscopic crystalline particles, oriented with respect to the fibre axis, and separated from one another by amorphous cementing material which coheres, yet allows the micelles to move as a unit during intermicellar swelling and plastic flow, and also to be dispersed during the early stages of the solution process. The essential attribute of the continuous-structure theory is the existence of long cellulose chains which have crystallized out as best they can in the cell membrane in such a way that the crystalline regularity in the membrane is intercepted by warped or irregular regions which behave essentially as amorphous material toward X-rays and toward the penetration of swelling and dispersing liquids. The essential attribute of the cellulose-particle theory is the existence of imperfect crystalline cellulose particles oriented with respect to the fibre axis, and separated from one another by amorphous pectic materials which cohere yet allow the particles to move as units during intermicellar swelling and plastic flow, and also to be dispersed as a unit during the early stages of the solution process.

It has been suggested [18] that, with the exception of size and shape, the essential features of the micellar and the particle theory are identical. If it is assumed that the particle has a continuous but imperfect crystalline structure (the essential feature of the continuous-structure theory) so as to account for the chemical data and the width of the diffraction line, then the major argument for the existence of long rod-like submicroscopic micelles in natural fibres ceases to exist.

Perhaps we may think of the crystallinity of a natural fibre as being discontinuous, in that the cell membrane is built up of fibrils formed by bead-like strands of cellulose particles; on the other hand the crystallinity is continuous, in that the particle has a continuous but imperfect crystalline structure. Such a concept appears to explain not only the X-ray data (fine structure) but also the microscopic data (gross structure) which reveals the presence of a spiral structure in many fibres. The "*crystallite*" which gives the broad Debye-Scherrer diffraction lines, and which behaves as a unit during swelling and plastic flow in natural fibres, may be the imperfect crystalline cellulose particle; the "*micelle*" or cellulose chain-aggregate which behaves as a unit in solution or as regenerated cellulose, may be a fragment of the disrupted particle, its dimensions a function of the dispersion process.

In conclusion may it be emphasized that this picture of the crystallite is purely hypothetical. It is hard to see, in the light of our present experimental methods, how any concept of the fine structure of cellulose can be otherwise. The final verdict regarding the structure of the cellulose crystallite, therefore, must await the advent of further circumstantial evidence.

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Textile Foundation Research

AT a meeting of the Directors of the Textile Foundation, held in Washington, D. C., Dec. 10, it was decided to continue the program of scientific research on problems related to the textile industry and the production of textile fibres for another year. Although in many cases the title does not adequately describe the scope of the work of Foundation Fellows, or the specific approach to certain research aspects, the following list indicates the nature of their work and where it is being carried on:

Adsorption and Absorption of Solutions by Textile Materials. John B. Calkin, Cornell University.

Disposal and Recovery of Textile Wastes. Maxwelton S. Campbell, University of North Carolina.

Effect of Bacteria and Vegetable Oils on Silk. A. J. Frantz, Lehigh University.

Fundamental Study of Silk. Mearl A. Kise, Yale University.

Application of Polarized Light to Textile Research. Donald R. Morey, Cornell University.

Application of the Spectrophotometer in Solution of Textile Problems. Robert D. Nutting, Massachusetts Institute of Technology.

Quantitative Method for Describing the Rate of Exhaust in Continuous Dyeing. John S. Reese IV, Massachusetts Institute of Technology.

Protective Effects in Textile Deterioration and Dye Fastness. Donovan J. Salley, Princeton University.

X-ray Analysis of Fibres. Wayne A. Sisson, University of Illinois.

Biochemical Research on Silk. Werner Bergmann, Yale University.

Microbiology of Textile Fibres. Bryce Prindle, Massachusetts Institute of Technology.

Progress reports are periodically received from the fellows and are published in *Textile Research,* the monthly magazine of the United States Institute for Textile Research, Inc. Reprints of most of the reports are available on application to the Foundation.

The Directors received progress reports on several studies now under way, including the following subjects:

(1) The Training of Men for the Textile Industries. The educational study has received whole-hearted support from the textile school heads, who have developed a program of semi-annual conferences for the purpose of adapting textile educational courses and practices to meet changing demands.

(2) Flax Production, Preparation and Utilization. Flax was planted

Continued on page 148

Silk Degumming

II.—The Rate of Degumming Silk

By H. W. WOLF * and O. A. HOUGEN †

Abstract

The mechanism of silk degumming in soap or alkaline solutions may be represented by the general equation

$$\frac{dS}{d\theta} = -(c + kA)S$$

where *S is the sericin content of silk, expressed in grams per gram of dry, clean silk.*
A is the gram equivalents of alkali present in the bath per gram of dry, clean silk.
c is the degumming coefficient in water alone.
k is the degumming coefficient due to the presence of soap or alkali.

The coefficient k is dependent upon temperature, yarn size, degree of agitation, water-silk ratio, and nature of soap or alkali. For small laboratory tests conducted at the normal boiling-point, at constant weight, on 140 denier knitted tubing with a water-ratio of 100 to 1 the values of k were found to be as follows for the various alkalies and to be nearly independent of concentration:

Sodium hydroxide	*984*
Sodium carbonate	*873*
Sodium silicate (SiO_2/Na_2O ratio 3.73)	*427*
Trisodium phosphate	*349*
Borax	*189*
Sodium bicarbonate	*173*

For soap solutions the values of k decreased with increasing normality of soap and may be represented by the equation

$$\log_{10} k = 2.806 - 15.4N_0$$

where N_0 is the initial normality of the soap solution. Under the given experimental conditions the minimum time

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of degumming is obtained in a soap solution having a normality of .029. The binding weight of sericin to be used in calculating the alkali or soap consumed in degumming was found to be about 1600.

Theory of Degumming Silk

PERHAPS no other phase of silk technology has been more thoroughly investigated than the simple process of removing sericin from the silk fibre. For hundreds of years methods of silk degumming have been well known. The practice has not changed much during the last century. The data of experimental tests have usually been left in the form of graphs or tables without receiving any formulation in terms of the mechanism of the reactions involved. The present investigation is unique in that an attempt is made to formulate mathematically the fundamental laws underlying the mechanism of degumming silk by alkalies consistent with experimental evidence.

In a previous paper [5] the chemical composition and properties of sericin were discussed. As it exists on the silk fibre sericin is said to coat the filaments in three distinct layers.[3a] The outer layer consists of sericin A, which is elaborated by small glands in the silk-worm auxiliary to the main silk glands. The remaining sericin consists of sericin B produced by the main glands of the silk-worm. Any pigment present is stratified near the common boundary. Recently, Mosher [3] stated that an innermost layer of sericin, called sericin C, is particularly resistant to enzymic action. Takahashi [4] states that alkaline degumming consists, first, in glutinization whereby the sericin particles become hydrated and charged with hydroxyl ions; the second step consists in the dispersion of the glutinized particles by the repulsion of similarly charged particles; the third step is called a secondary albuminate formation whereby the dispersed particles are further stabilized by hydrolysis. To the authors it seems that the degumming of silk is a chemical reaction, rather than one depending principally upon absorption and diffusion. The principal argument for the chemical theory is the very high temperature coefficient of reaction rate. The experimental data reported by the Textile Research Division of Procter and Gamble [1] and by Mosher [3] show that the rate of degumming is more than doubled by a 10° C. rise in temperature, thus indicating the chemical nature of the process. The reduction of active alkali content during degumming, the formation of free oleic acid from reaction with soap, and the liberation of carbonic acid by reaction with sodium carbonate are further evidences of chemical reaction. The chemical reaction is complicated by the presence of at least two sericin fractions and by the progressive degradation of the sericin particle after it enters solution.

Following its removal from the silk the resultant alkali-sericin compound undergoes progressive decomposition in combination with more alkali. As pointed out in a previous paper [5] the binding weight of the sericin continually changes as this decomposition progresses until an equilibrium value is attained.

Based upon experimental observations, and a knowledge of the composition of sericin and its distribution over the silk filament, the following mathematical formulation of the fundamental principles involved seems plausible.

Consider raw silk yarns of a given size made up into a uniform fabric and degummed under definite conditions of temperature, agitation and support. The rate of degumming at any instant is proportional to the instantaneous alkali ratio in the bath and to the active surface of sericin exposed. It would seem at first thought that the area of the sericin exposed would be constant and equal to the total surface of the silk filaments. Actually the area of sericin exposed seems to be proportional to the sericin present; that is, the active surface progressively diminishes as the sericin is removed. It seems that the sericin actually goes off in points leaving a submicroscopic network of sericin which is ever shrinking in area as degumming proceeds. An exactly analogous situation is encountered in the drying of a textile where diffusion rates are high. Besides the removal of sericin by chemical reaction with alkali, sericin is also slowly peptized by hot water. The two reactions proceed simultaneously. With this understanding the rate of degumming may be expressed by the fundamental equation:

$$\frac{dS}{d\theta} = -(c + kA)S \tag{1}$$

where S = sericin content of silk at any time, θ, expressed in grams per gram of dry, sericin-free silk.
θ = time elapsed, in minutes.
A = instantaneous concentration of alkali, in gram equivalents per gram of dry, sericin-free silk.
c = degumming coefficient produced by action of water alone.
k = degumming coefficient produced by soap or alkali in solution.

From a weight balance of alkali consumed and of sericin removed the following equation results:

$$A_0 - A = \frac{S_0 - S}{B} \tag{2}$$

where A_0 = initial alkali concentration of bath expressed in gram equivalent per gram of dry, clean silk.
S_0 = initial sericin content of silk, in grams per gram of dry, clean silk.
B is the binding weight of sericin; the number of grams of sericin uniting with one gram equivalent of alkali as the sericin just enters into solution.

By examination of equations (1) and (2) it will be observed that three constants appear which must be experimentally determined; namely, B, c, and k. The coefficient c can be determined by making an experimental degumming test with distilled water alone, coefficient k can best be determined by degumming at fairly high concentrations so that the alkali concentration remains nearly constant throughout the period of the run. The binding weight, B, can be determined by degumming with a concentration of alkali sufficiently low to note the progressive decline in the rate of degumming as the consumption of alkali proceeds. The degumming coefficients c and k are dependent chiefly upon temperature, but also upon the degree of agitation of the bath, size and construction of yarn and fabric and the method of support in bath. In addition to these variables the degumming coefficient is dependent upon the kind of alkali and soap, and possibly upon the concentration, or pH, of the bath.

It is the purpose of the present investigation to test the validity of Equation (1) and to evaluate the degumming coefficient k in terms of its controlling variables.

Experimental Procedure

Experiments were conducted on a laboratory scale employing one gram samples of silk tubing knit from ten-thread silk, averaging 140 deniers. The samples were first freed from reagents which had been added in soaking the raw silk by resoaking overnight in cold distilled water. Practically all the reagents were removed by this soaking. The samples of tubing were stretched evenly over nickel-wire frames to permit uniform action of the boil-off bath. One hundred grams of solution were used for each gram of silk (dry basis, with original sericin content).

The solution of desired composition was placed in a wide-mouth assay flask of 500 cc. capacity, heated and maintained at the boiling-point by an electric hot plate, and attached to a special copper reflux condenser to maintain constant water content in the bath. The heater and condenser were designed to accommodate eight flasks at once so that a series of time tests for each composition of boil-off bath could be conducted simultaneously. With each solution, tests were conducted in duplicate and for various time intervals. After boiling was attained the silk samples were added and the degumming continued for the allotted time.

The samples were then quickly withdrawn from the boil-off bath, plunged into cold water and rinsed ten times by alternate squeezing and soaking in a stream of cold distilled water. The samples were rinsed once in ether and once in alcohol to remove traces of soap or fatty acid when soaps were used in degumming. The samples were air-dried and then oven dried for two hours at 220° F. The dry weight of the sample was obtained by direct weighing in the oven. The sample was completely degummed by boiling-off in a 1% soap solution for one-half hour and repeated again for one-half hour in a fresh soap bath. The sample was again rinsed in alcohol and ether and its dry weight recorded as before. The initial weight of the sample was obtained by measuring in the conditioned state, obtaining the moisture content on separate samples which were not used for degumming tests. All calculations of sericin and alkali contents of the bath were converted to the basis of one gram of dry sericin-free silk. The pH of the boil-off bath was measured at 20° C. before and after each test. Measurements were made with a Leeds and Northrup glass electrode in conjunction with a sensitive galvanometer.

Evaluation of c, the Degumming Coefficient in Water Alone

When silk is degummed by hot water alone the general Equation (1) reduces to

$$\frac{dS}{d\theta} = -cS \tag{3}$$

By degumming in distilled water at the normal boiling-point values of S were determined experimentally at successive time intervals. By plotting values of $\log_{10} S_0/S$ against time, a straight line results, the slope of which is equal to c/2.303. From the data recorded in Table 1, Run 45, the value of c was found to be 0.0047.

TABLE 1

Degumming with Distilled Water-Run 45
Initial pH = 6.7 Average S_0 = .224
Average pH = 6.7 c = .0047

Time Minutes θ	←Dry Weight of Silk→ Before	After	Total ←Degumming→	pH at Time θ	S_0	S	$\frac{S_0}{S}$
5	1.5332	1.5088	1.2442	6.65	.232	.204	1.14
5	1.4655	1.4474	1.2072	6.65	.214	.199	1.18
10	1.4874	1.4576	1.1981	6.5	.241	.208	1.16
10	1.4125	1.3852	1.1572	6.5	.221	.197	1.12
20	1.4887	1.4516	1.2196	6.5	.220	.1905	1.15
20	1.3865	1.3590	1.1332	—	.223	.199	1.12
40	1.5350	1.4516	1.2592	6.65	.219	.175	1.25
40	1.4374	1.3877	1.1678	6.65	.230	.188	1.23
80	1.5258	1.4797	1.2490	6.70	.222	.156	1.42
80	1.4554	1.3902	1.1974	6.70	.215	.161	1.34

Evaluation of B, Binding Weight of Sericin

In a previous paper[5] values of the binding weight of sericin towards alkalies were summarized by the equation

$$B = -1000 \log_{10} R - 2180 \qquad (4)$$

where R is the initial ratio of gram equivalents of alkali per gram of total sericin initially present. However this equation represents the total weight of sericin decomposed by one gram equivalent of alkali in attaining a point of equivalence corresponding to a pH value of about 9.8. At this point the alkali-sericin is still capable of further degumming. The values of B obtained from Equation (4) really represent the progressive degradation of sericin in the alkaline bath after its removal from silk, and apparently do not represent the alkali reacting as the sericin just enters solution. To determine the value of B just as the sericin enters solution degumming tests were conducted with a low concentration of caustic soda and continued until the rate of degumming became and continued equal to that of degumming in distilled water. When values of $\log_{10} S_0/S$ were plotted against time the slope of the curve decreased gradually as alkali was consumed; when the slope became equal to that of degumming in distilled water it was assumed that all alkali had reacted and a corresponding value of B = 1550 was obtained (Fig. 1). A better procedure is first to establish a value of the degumming coefficient k for NaOH by degumming at a fairly high concentration of alkali such that little appreciable change in alkali concentration occurs. It will be subsequently shown that for alkalies the value of k is nearly independent of concentration. Knowing values of k and c, the value of B can then be determined by degumming in a low concentration

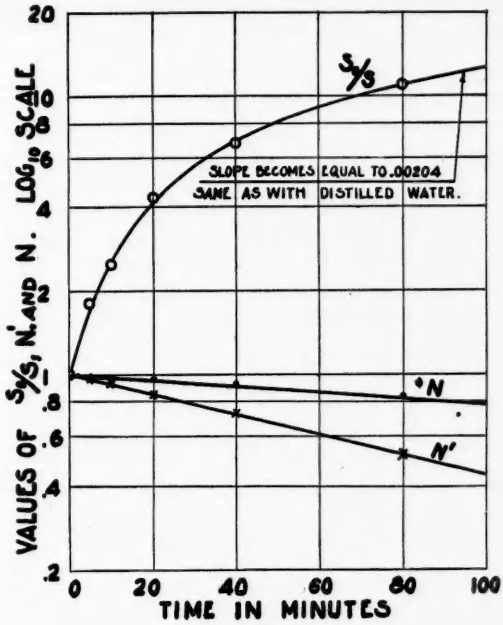

FIG. 1. Degumming with low alkali concentration. Run No. 19. .0012N NaOH. $A_0 = .000149$; $c = .0047$; $K = 984$.

such that nearly all the alkali is consumed during the course of the reaction. Upon integration of Equation (1) the following results:

$$2.3 \log_{10} \left\{ \frac{S_0}{S} \frac{(c + kA)}{(c + kA_0)} \right\} = (c + ak)\theta \tag{5}$$

where

$$a = A_0 - \frac{S_0}{B} \tag{6}$$

In Run 19, degumming with 0.0012N NaOH, the following results were obtained:

Time	S	S_0/S
0	.250	1.00
5	.139	1.80
10	.101	2.49
20	.0576	4.34
40	.0366	6.84
80	.0227	11.0

For this run, $c = .0047$; $k = 984$; $S_0 = .250$; $A_0 = .000149$. Values of B can be obtained by substituting known values in Equations (5) and (6) and solving for B.

The following equation and resultant values of B were obtained for different time periods:

Time Minutes	Reduced Equation	B
5	$\log_{10}\left(1 - \frac{718}{B}\right) = -\frac{545}{B} + .075$	1630
10	$\log_{10}\left(1 - \frac{974}{B}\right) = -\frac{1070}{B} + .264$	1600
20	$\log_{10}\left(1 - \frac{1240}{B}\right) = -\frac{2140}{B} + .683$	1620
40	$\log_{10}\left(1 - \frac{1380}{B}\right) = -\frac{4280}{B} + 1.804$	1600
80	$\log_{10}\left(1 - \frac{1470}{B}\right) = -\frac{8550}{B} + 4.328$	1600

Highly reliable data on the values of B and its possible variation with alkali concentration are as yet not available. In all tests where little change in alkali or soap concentration occurs during reaction it was found safe to use an average value of 1600 in evaluating the coefficient k. The experimental data on determining binding weights are shown graphically in Fig. 1.

Evaluation of Degumming Coefficient k

By avoiding extremely dilute solutions reliable values of k may be obtained even though values of B are not known to a high degree of precision.

Equation (5) may be written

$$2.3 \log_{10} N = (c + ak)\theta \tag{7}$$

where

$$N = \left(\frac{c + Ak}{c + A_0 k}\right)\frac{S_0}{S} \tag{8}$$

Where c is small compared to Ak, Equation (8) reduces to

$$N' = \frac{S_0}{S}\frac{A}{A_0} = \frac{S_0}{S}\frac{\left(a + \frac{S}{B}\right)}{A_0} \tag{9}$$

Hence,

$$2.3 \log_{10} N' = (c + ak)\theta \tag{10}$$

By plotting values of log N′ against θ, a straight line is obtained the slope of which is equal to $(c + ak)/2.3$. From known values of a and c the values of k are calculated. Where values of c are not negligible compared to Ak it will be convenient to determine an approximate value of k by the preceding method, then by substituting the approximate value into Equation (8) and plotting values of $\log_{10} N$ against θ a correct value of k may be obtained. However, this procedure is not reliable at extremely low concentrations because values of k are dependent upon values of a; at low concentrations values of a are obtained as the difference between two large num-

bers; small errors in either will introduce a very large error in the value of a.

A comparison of the logarithmic plots of S_0/S, N′ and N is shown in Fig. 1. Except for very low concentrations, the N and N′ plots are nearly the same. In cases of degumming with alkali where no appreciable change in alkali concentration occurs all three plots become identical.

Degumming Coefficients with Soap

Degumming tests were conducted with a series of soap solutions of different initial concentrations and the values of k determined as described. Experimental data are shown graphically in Fig. 2. The summarized results are given in Table 2.

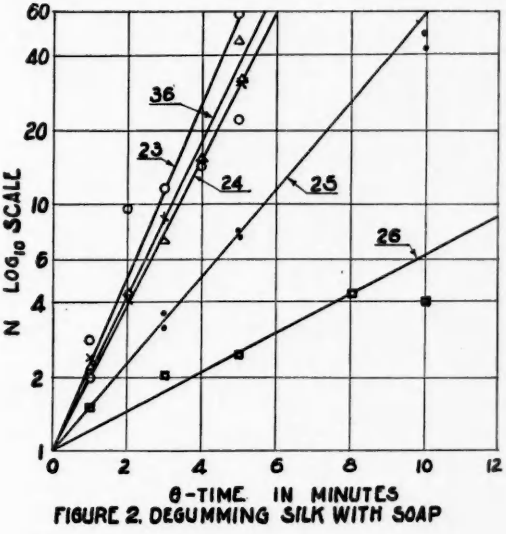

FIGURE 2. DEGUMMING SILK WITH SOAP

TABLE 2

Summary for Soap Solutions

Run	Initial Normality	Values of pH Initial	Average	k
23	.032 N	10.5	10.2	208
36	.025	10.4	10.0	247
24	.016	10.35	10.2	373
25	.008	10.3	10.2	482
26	.004	10.2	10.0	516

From these data it is evident that the degumming coefficient is independent of the average pH of the bath and decreases markedly with increasing concentration of soap. When values of $\log_{10}$ k are plotted against the initial normality of the soap solution a straight line plot results (Fig. 3).

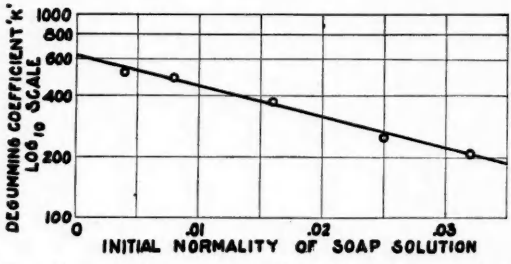

FIG. 3. Variation of degumming coefficient k with normality of soap solution.

For soap solutions the degumming coefficient can be expressed by the equation

$$\log_{10} k = 2.806 - 15.4\ N_0 \tag{11}$$

where $2.806 = \log 640$ which is equal to the intercept of the line at zero normality, and -15.4 is equal to the slope of the line (Fig. 3). N_0 is the initial normality of the soap solution. In natural logarithms Equation (11) becomes

$$\ln k = 6.46 - 35.4N_0 \tag{12}$$

It is important to point out that the degumming coefficient is a measure of the rate of degumming only under given conditions of soap or alkali concentration and sericin content. Because of the influence of soap concentration upon k the rate of degumming in soap solution does not increase directly with an increase in soap concentration but at a rate less than direct proportionality.

The soap concentration giving the most rapid rate of degumming, or accomplishing degumming in the least time, can be calculated mathematically by equating to zero the derivative of the time of degumming with respect to normality, or

$$\frac{d\theta}{dN} = 0 \tag{13}$$

The time of degumming is given by Equation (5). Under practical conditions of boiling-off the value of c is negligible and A is nearly constant during the course of a single run; hence Equation (5) reduces to

$$\theta = \frac{\ln \frac{S_0}{S_1}}{\alpha k N_0} \tag{14}$$

where α is the proportionality factor relating the normality, N_0, and A. Substituting the value of k from Equation (12) into Equation (14), and differentiating, the following results:

$$\frac{d\theta}{dN_0} = \frac{\ln \frac{S_0}{S_1}}{\alpha k N_0}\left[35.4 - \frac{1}{N_0}\right] \tag{15}$$

Since $d\theta/dN_0$ equals zero at the minimum time of degumming,

$$N_0 = \frac{1}{35.4} = 0.028 \tag{16}$$

Hence, for the particular conditions involved in these experiments the maximum rate of degumming is obtained with a soap normality of .028.

The increasing effectiveness of soap in degumming silk with increased dilution is consistent with the greater hydrolysis of soap at low concentration, and with the fact that soap gradually loses its colloidal properties and approaches the behaviour of a true solution as its dilution is increased.

Effect of Various Alkalies

It was discovered that, with sodium carbonate as well as with sodium hydroxide solutions, the degumming coefficient, k, was independent of concentration (Figs. 4 and 6). By plotting the slopes of $\log_{10} N$ obtained

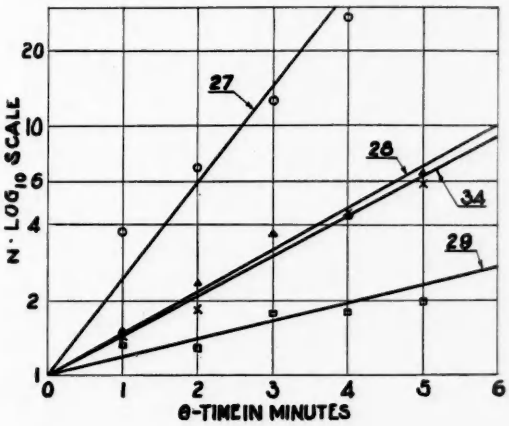

FIG. 4. Degumming silk with sodium carbonate.

for each run of different alkali concentration against values of θ, a straight line was obtained for each alkali (Fig. 5). The general equation

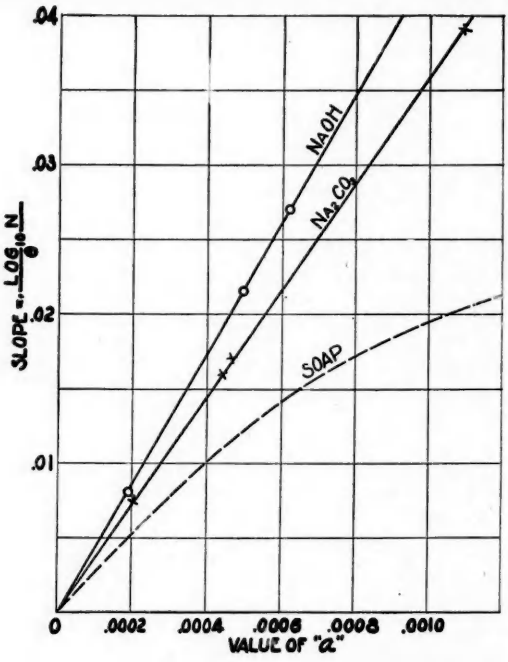

FIG. 5. Evaluation of degumming coefficient k.

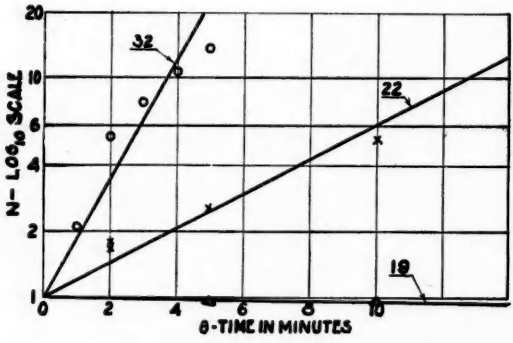

FIG. 6. Degumming silk with sodium hydroxide.

of these lines is

$$s = \frac{c + ak}{2.3} \tag{17}$$

where s is the slope and c, a and k have their usual significance. The intercept of the line is equal to c/2.3, and its slope to k/2.3. By this procedure the average k for sodium hydroxide was found equal to 984 and for sodium carbonate 827.

The degumming coefficients were likewise obtained for sodium bicarbonate, borax, sodium silicate and trisodium phosphate. Experimental data are recorded in Fig. 7.

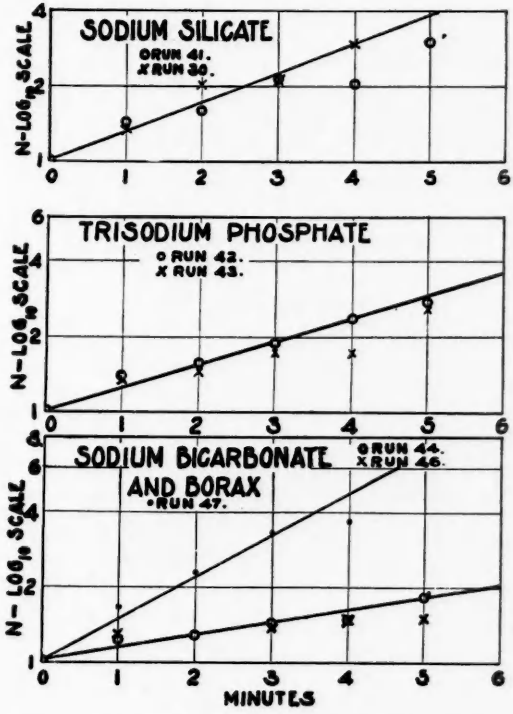

FIG. 7. Degumming silk with various alkalies.

Summary of Experimental Data

The experimental data of all tests are summarized in Table 3.

TABLE 3

Summary of Experimental Data

Run No.	A_0	Initial Normality	Values of pH Initial	Values of pH Average	k
Soap					
23	.00402	.032	10.5	10.2	208
36	.00301	.025	10.4	10.0	247
24	.00200	.016	10.35	10.2	373
25	.000996	.008	10.3	10.2	482
26	.000503	.004	10.2	10.0	516
NaOH				Average k from curve =	984
32	.000764	.00625	—	11.7	986
18	.000649	.00514	12.1	11.2	978
22	.000346	.00275	11.5	10.5	906
19	.000149	.00120	11.0	9.4	984
Na_2CO_3				Average k from curve =	827
27	.001233	.010	12.35	11.6	831
28	.000627	.005	11.8	10.9	821
34	.000565	.0047	—	10.25	826
29	.000342	.0028	11.7	10.8	802
Sodium Silicate—($SiO_2/Na_2O = 2.6$)					
30	.000755	.0062	10.05	9.9	427
41	.000761	.0062	10.05	9.9	427
Trisodium Phosphate, Na_3PO_4					
42	.000705	.00576	11.25	10.3	349
43	.000718	.00576	11.25	10.3	349
Borax					
47	.00252	.0176	9.1	9.0	189
Sodium Bicarbonate, $NaHCO_3$					
44	.000831	.00671	8.15	9.1	173
46	.000828	.00671	8.15	9.1	173

The relative decreasing order of effectiveness of different alkalies in degumming silk upon the basis of equivalent weights is as follows:

Sodium hydroxide	984
Sodium carbonate	827
Sodium silicate ($SiO_2/Na_2O = 3.73$)	427
Trisodium phosphate	349
Borax	189
Sodium bicarbonate	173

For each of these alkalies the value of the coefficient seems to be nearly independent of concentration or pH. However, for the different alkalies

the degumming coefficients are approximately proportional to their relative alkalinities as measured by pH. In degumming with sodium bicarbonate the pH of the bath increases progressively; this is further evidence of chemical reaction with sericin, the release of carbonic acid and formation of sodium-sericin increasing the akalinity or pH of the bath.

Soap varies in its degumming coefficient from 208 to 516, as its normality is decreased from .032 to .004 N.

Criticisms

Attempts were made to correlate the experimental data in silk degumming upon the basis of other mechanisms and other mathematical theories, but the proposed theory is the only one which adequately correlates the facts. Much difficulty is experienced in obtaining results with high precision because of the many vagaries of silk; unexpected variations occur in sericin content, diameter of filament and nature of sericin. Sericin, like other proteins, is easily denatured or altered in its chemical behaviour. Whereas all tests were conducted at nearly constant temperature, variations in the degree of agitation, even in a boiling bath, greatly influence the values of degumming coefficients. Variations in the supply of heat to the reaction vessels will alter experimental results, even though the temperature of bath is kept constant. This is because an increased heat supply causes increased agitation and hence results in an increased value of the coefficient. A value of the binding weight of sericin as it just reacts with alkali was found to be 1600; whether or not this value varies appreciably with concentration of alkali has not been definitely established. The method of rinsing the partly degummed silk is also open to criticism; the alternate squeezing and soaking of silk skeins may cause some mechanical loss of sericin.

In a subsequent paper the extension of the proposed theory will be applied to the boiling-off of silk hosiery, and degumming coefficients will be obtained for practical plant conditions. Also in this subsequent paper the theory and tests will be extended to show the effects of temperature, mixtures of soap and alkali, agitation, yarn size, size of machine and loading or water-silk ratio under practical boil-off conditions.

Conclusions

1. A theory has been built up with mathematical formulation describing the chemical kinetics of silk degumming.

2. The degumming coefficients of alkalies are nearly independent of concentration and are specific for each reagent.

3. On laboratory tests conducted at the normal boiling-point the degumming coefficients of different alkalies on ten-thread silk, with a water ratio of 100 to 1, are as follows:

NaOH	984
Na_2CO_3	827
Sodium silicate ($SiO_2/Na_2O = 3.73$)	427
Trisodium phosphate	349
Borax	189
Sodium bicarbonate	173

4. In soap solutions the degumming coefficient decreased with increasing concentration of soap, varying from 516 for .004 N soap to 208 for .032 N soap. The degumming coefficient is independent of the pH of the bath.

5. Value of binding weight for sericin as it just reacts with alkali was found to be 1600. This value does not refer to the binding weight of sericin as it continues to decompose in the bath after its removal from silk.

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3. *Ibid.*, *49*, 7, 53–6; *49*, 8, 54–6, 62; *49*, 9, 59–60 (1930).
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Editor's Note. Tabulated data upon which diagrams are based may be obtained, if desired, by addressing O. A. Hougen, United States Testing Co., 1415 Park Ave., Hoboken, N. J.

Textile Foundation Research

Continued from page 133

in fifteen different localities principally along the Atlantic seaboard. Careful records were made of the harvest and production costs. The straw was then shipped to Clemson College, S. C., where, under the direction of H. H. Willis, it was run through preparatory machines. Experiments are now being conducted on the utilization of this fibre on cotton and worsted machinery, and for paper making.

(3) Regional Variety Tests on Cotton Production. The experiments on the community production of limited types of cotton were conducted over the cotton belt, under the auspices of the Bureau of Plant Industry of the Department of Agriculture, and an analysis of the results is now being made.

A proposal to engage in research on the warp sizing of cotton and synthetic fibre yarns was acted on favorably, and a co-operative program of work will soon be started under the auspices of the United States Institute for Textile Research.

The office of the Textile Foundation is located in the Commerce Building, Washington, D. C., and the Directors are: Franklin W. Hobbs, chairman; Stuart W. Cramer, treasurer; Henry A. Wallace, Secretary of Agriculture; Daniel C. Roper, Secretary of Commerce; Frank D. Cheney, and Edward T. Pickard, secretary.

Methylene Blue Absorption as a Quantitative Measure of Wool Damage

By RUTH E. ELMQUIST* and OLIVE P. HARTLEY†

Abstract

The absorption of methylene blue from buffered solutions is proposed as an index to wool deterioration, since it can be measured quantitatively by a simple titrimetric procedure. Experimental results are given for material damaged progressively under controlled conditions of laundering, and for fabrics containing wools of different grades and different dyeings. A linear relationship was found to exist between absorption and tensile strength. The reworked wool that was tested absorbed nearly four times as much methylene blue as the new serge used in the experiments. Optimum test conditions were determined and are discussed critically.

THE methylene blue absorption method described here for estimating the soundness of wool was developed in connection with a study of the chemical changes occurring in woolen blankets as a result of wear and laundering. A chemical test for measuring deterioration in wool is important since wool is liable to be damaged in the various acid, alkaline, oxydizing, and reducing processes it undergoes during manufacture and since such large quantities of worn wool are reworked and marketed as new material.

Review of Literature

Methylene blue has been used by Kertess [8] and Sommer [14] in studying the effect of weathering on wool, and by von Bergen [2] in experiments on the effect of light. They found that the exposed wool was dyed a deeper shade than the untreated material. Ristenpart and Schwerdtner [13] observed also that bleaching methods affected the amount of methylene blue taken up in subse-

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quent dyeing. Pelet-Jolivet and Andersen [12] reported that the amount of methylene blue fixed by the same weight of wool was variable.

The first attempt to obtain results that could be expressed quantitatively was made by Kronacher and Lodemann [9] who dyed wool with methylene blue and counted the dyed, partly dyed, and undyed fibres under the microscope, using the count as an index of damage. The method is at best laborious, and introduces special sampling difficulties, since such small quantities are used for each count. In addition, it cannot be used for dyed or felted wool.

No reference to a volumetric method for determining damage in wool by means of dyestuffs has been found in the literature. The method described here is a simple titrimetric procedure which gives accurate, reproducible results and which can be used on fabrics or raw wool and on undyed or dyed materials. Wool in finished garments can also be tested by this method since enough material to make the determination can be cut from seams. Only 0.1 g. is needed for each analysis.

Materials

In order to correlate methylene blue absorption measurements with breaking strength determinations, absorption tests and warp breaking strengths were made on a series of fabrics which was prepared by damaging a white serge material to various definite extents in an experimental washer. Serge of high initial breaking strength was used, since washable wool materials such as flannels and blankets have low tensile strength. The serge is a bleached, clear-finished, 2/2 even twill weighing 8.5 ozs. per square yard. Other methylene blue tests were also made on fabrics composed of wools of different grades, on materials of dyed wool, and on a wool and cotton mixture.

Method for Producing Deterioration

Ten-inch squares of the serge are damaged by prolonged laundering in an experimental cylinder washing machine, each run lasting 17 hours. The capacity of the machine is such that three squares constitute a load and 7 l. of suds give a high suds level. The machine is run at 18 r.p.m., reversing every three revolutions to reduce mechanical damage. The serge is entered into .25% castile soap suds at room temperature and the suds brought to 37° C. in the first hour, after which it is held at this temperature for the remaining 16 hours by a thermoregulator. After each run the squares are rinsed six times, the temperature of the first rinse being 37° C. and each subsequent rinse about 2° lower. Distilled water is used throughout. It will be noted that the conditions prescribed are the ones generally accepted as producing minimum damage in wool laundering, except for the two factors of prolongation of the process and the use of a cylinder machine. The cylinders are so small, however, and run at such slow speed that it is doubtful whether the mechanical damage is any greater than it would be in a Y-pocket machine of normal size.

Physical Tests

The procedure used for breaking strength measurements is as follows: Strips are cut 1¼ by 6 ins., raveled down to exactly 1 in., and broken under

standard conditions of humidity and temperature with a Scott tester which has a 3-in. back and front jaw and a distance between the top and bottom jaws of 3 ins., the lower jaw traveling down at the rate of 12 ins. per minute. Warp specimens are broken and the average of 10 readings reported in each case.

After damaging, the serge appears stronger than it actually is, as a result of shrinkage. In order to compensate for this effect the index value, that is, the average breaking strength in pounds divided by the average thread count, is computed. The threads in the laundered serge samples are so closely packed that it is impossible to count them with a thread-counting micrometer. Consequently they are counted with the aid of a dissecting needle and a magnifying glass in the strips which have been raveled down to 1 in. for the breaking strength measurements. In each case the value reported is the average of 10 readings.

Procedure for Absorption Measurements

The samples of woolen fabrics, or cleaned raw wool, are first given an acid wash similar to that recommended by Clibbens and Geake[6] in their investigation of the absorption of methylene blue by cotton. This acid wash consists in steeping the wool in N/10 HCl for 1 hour, washing 12 times with distilled water, steeping in water for about 3 hours, washing 12 more times with distilled water, and drying at room temperature. Since wool absorbs acids strongly, HCl is substituted for the N/10 H_2SO_4 used by Clibbens and Geake[6] in order to take advantage of the volatility of HCl. The purpose of the acid wash is to remove any soap which may be present in laundered fabrics and to obtain a minimum ash alkalinity. Clibbens and Geake[6] found that even in buffered solutions the absorption of methylene blue is affected to some extent by the ash content of cotton, or, more probably, the alkalinity of the ash.

After the acid washing, the wool is finely divided in a special non-heating mill with a cutting action until it passes a 1 mm. sieve enclosed in the mill. The disintegrated material is conditioned overnight at 70° F. and 65% relative humidity, and 0.1 g. samples weighed out into narrow glass tubes stoppered at both ends.

Exactly 15 cc. portions of methylene blue solution are measured into 40 cc. centrifuge tubes and the wool samples transferred from the narrow glass tubes into these solutions with the aid of a stirring rod. The centrifuge tubes are stoppered and allowed to stand for 24 hours. The solution is then separated from the wool by centrifuging and 10 cc. of it pipetted off and titrated against naphthol yellow S.

One molecule of naphthol yellow S couples with two of methylene blue, forming a reddish brown precipitate which settles so slowly that it is necessary to centrifuge the mixture shortly before the end of the reaction, in order to observe the color change of the solution. Since this change in color from blue to yellow is not abrupt, the titrations are continued until the color of the solution matches a sample used for comparison, which has been titrated to the bluish-green stage. These titrations can be carried out rapidly and the end point easily determined within 0.03 cc.

The absorption of methylene blue in millimols per 100 g. of dry wool is calculated from the difference of titer of 10 cc. before and after immersion of the wool. All methylene blue absorption measurements are carried

out in duplicate. Moisture content determinations are made on the wool samples using the procedure and specially designed bottles described by Barritt and King.[4]

A neutral (pH7) buffered, m/250 solution of methylene blue is used. It is prepared as recommended by Clibbens and Geake[6] and contains 1.279 g. of methylene blue hydrochloride, 6.81 g. of potassium dihydrogen phosphate, and 29.63 cc. of normal sodium hydroxide solution in 1 l. of solution. The methylene blue hydrochloride used for the solution is recrystallized three times from water and air dried. The dye content of the crystals is determined by titration with titanium chloride according to the procedure of Calcott and English,[5] and the moisture content by drying a sample to constant weight at 110° C. A solution of naphthol yellow S containing 0.6 g. of the salt per liter is used to titrate the solution of methylene blue. Birtwell, Clibbens, and Ridge[3] state that the naphthol yellow S, itself, can be used as the ultimate standard in the analysis of methylene blue since it is readily purified.

Discussion of Procedure

Absorption measurements obtained by using the procedure are plotted in Fig. I for the new serge and for that which had been laundered in the

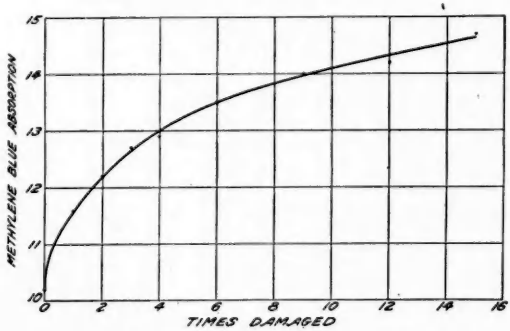

FIG. I. Methylene blue absorption of a serge fabric subjected to various periods of damage.

experimental washer for various periods. The curve shows that methylene blue absorption increases with laundering. The rate of this increase diminishes as the washing continues.

The values for warp breaking strength, warp thread count, and warp index of the new and laundered serge were determined and in Fig. II the absorption results are plotted against the index figures. A linear relationship exists between these two quantities. As the strength of the serge decreases the absorption steadily increases. Absorption determinations are more accurate than breaking strength tests and require much less material.

The methylene blue absorption of fabrics composed of wools of different grades was also determined. A material consisting of one part fine

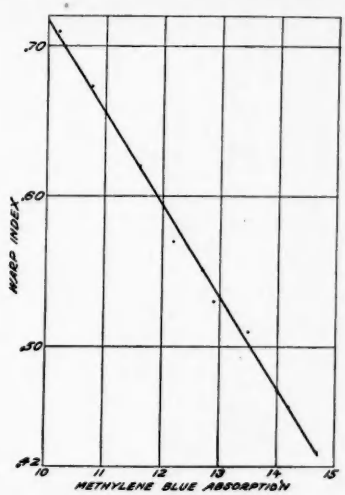

FIG. II. Relationship between methylene blue absorption and warp index of a serge fabric damaged to various extents.

$$\text{Index} = \frac{\text{Average breaking strength in pounds}}{\text{Average thread count}}$$

and one part half-blood wool gave an absorption value of 14.8, and one containing two parts ⅜-blood and one part ¼-blood, a value of 15.2. These results indicate that absorption varies with grade. A fabric made of one part ⅜-blood and two parts reworked wool, and another composed entirely of reworked wool were also analyzed. The figures, 31.8 and 40.4, respectively, were obtained, which show that the addition of reworked wool raises the absorption materially.

The average value found by this absorption method for the deviation from the average is 0.4%. This figure was obtained when analyses were made using the material which had been disintegrated in the special mill. For samples that have been sliced by hand, the average value for the deviation from the average is 1.1%. The same final result is obtained whether the material is disintegrated or sliced, although in the latter case equilibrium is reached more slowly. Although it is preferable to finely divide the wool, this absorption method may be used even when no mill is available.

When the volume of methylene blue is kept constant, absorption varies with the weight of wool taken for analysis. As the weight of the sample increases, absorption decreases. This decrease is small for fabrics with low absorption values but becomes progressively larger with the degree of deterioration of the fabric. (See Table I.)

Neale and Stringfellow[10] and Garvin, Griffiths, and Neale[7] state that at equilibrium the absorption of direct dyestuffs by cellulose decreases with rise of temperature. To find whether changes occurring in the laboratory

temperature would cause variations in our absorption results, measurements were made on several samples of wool at 70° F. and also at 100° F. In each case the differences obtained for the values at the two temperatures were within the limits of experimental error. Ordinary changes in room temperature apparently have no effect on the methylene blue absorption of wool.

In Fig. III the rates of absorption of methylene blue are given for three fabrics composed of wool of widely different absorption values. The

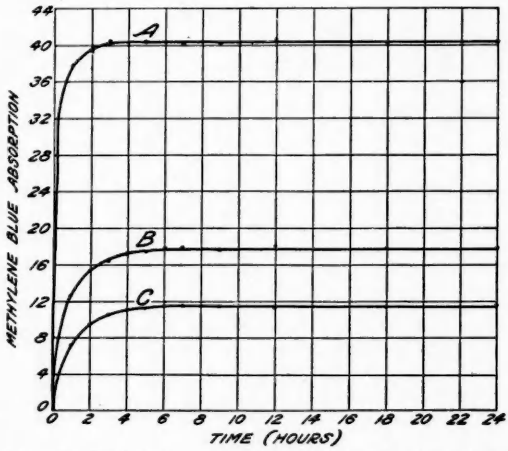

FIG. III. Rate of absorption of methylene blue by different wools: A, reworked-wool fabric; B, wool fabric, 1 part fine, 1 part ½-blood, given 12 ordinary launderings; C, serge fabric subjected to one period of damage.

badly damaged, reworked wool reached equilibrium in 3 hours, the less damaged wool in 5 hours, and the least damaged in 7 hours. The rate of absorption decreases as the absorption value decreases. Fig. III shows that the initial absorption of methylene blue by wool is rapid.

Since the wool which is most deteriorated comes to equilibrium first, a greater difference would be obtained for absorption values of different samples if less than equilibrium time were allowed for absorption. However, this advantage is offset by the greater accuracy possible when equilibrium is reached. Moreover, in the latter case, it is unnecessary to carefully regulate the time allowed for absorption.

In the method here described, the wool was allowed to remain in contact with the methylene blue solution for 24 hours. It is more convenient to add the wool to the methylene blue solution on one day and to separate and titrate the solutions on the following day, than it is to attempt to complete the operation in 8 hours.

An acid solution of methylene blue * was used for cotton by Clibbens

* This acid solution is m/250 and has a pH of 2.7. It is prepared by adding enough n/5 acetic acid to 1.279 g. of pure methylene blue hydrochloride to make 1 l. of solution.

and Geake [6] to supplement the tests made with the neutral buffered solution. The use of this acid solution fails entirely with wool because no absorption occurs. This finding is in accordance with the results of Briggs and Bull [4] and of Neville and Jeanson,[11] who state that the absorption of methylene blue by wool decreases as the solution becomes more acid.

To find whether this absorption method could be used for dyed materials, three colored, all-wool samples were tested before and after one, two, and three periods of prolonged agitation in the experimental washer. The absorption results for these fabrics are plotted in Fig. IV. The curves for

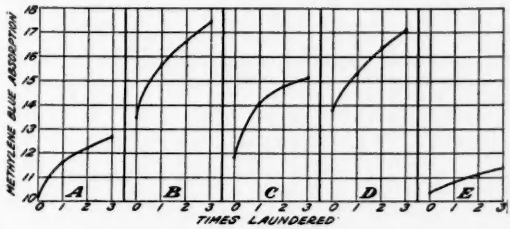

FIG. IV. Methylene blue absorption of undyed and dyed fabrics: A, undyed fabric, all wool; B, tan fabric, all wool; C, brown fabric, all wool; D, red fabric, all wool; E, green fabric, 50 per cent wool, 50 per cent cotton.

the dyed materials are similar to that previously found for the undyed serge. In both cases the absorption increases and the rate of this increase falls off as the washing continues. Apparently this method is as applicable to dyed as to undyed woolens. An important use for this test might be to disclose the degree of deterioration of the wool in some of the dyed reworked-wool products sold on the basis of being "all wool," but which are all reworked wool.

TABLE 1—EFFECT ON METHYLENE BLUE ABSORPTION OF VARIATION IN THE WEIGHT OF THE SAMPLES TAKEN FOR ANALYSIS

Weight	Reworked-wool fabrics	Methylene blue absorption	
		Wool fabric, 1 part fine, 1 part ½ blood	Serge fabric subjected to one period of damage
Grams			
0.05	43.8	15.4	11.9
.10	40.3	14.8	11.5
.20	31.3	13.7	10.9

In Fig. IV the absorption results are also given for a half wool and half cotton fabric when new and after one, two, and three periods of overnight agitation in the experimental washer. A part of the change in absorption is due to wool deterioration, a little to cotton, and some perhaps to a difference in proportion of wool and cotton in the worn goods as com-

pared with it when new. Combined with a test for percentage of wool in the mixture, this absorption method should give some key to the degree of deterioration of the wool in a mixed fabric. Such a test would be important because the condition of the wood in mixed materials is as important as the percentage of wool.

Authors' note.—Appreciation is expressed to Helen G. Wheeler for assistance with the chemical determinations and to Jeanne D. Guerin for making the breaking strength measurements.

Editor's note.—Tabular data for Tables 1–4 are available to those desiring them.

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Abstracts

This section is compiled under the direction of the Committee on Abstracts and Bibliography: Prof. E. R. Schwarz, Chairman, Dr. W. E. Emley, Prof. Louis A. Olney and M. W. Weiss.

I. Fibres (Synthetic and Natural) and Fibre Analysis

Animal Hairs: Constitution of. I. X-ray Interpretation. W. T. Astbury. *J. Soc. Dyers Col., Jubilee Issue* 1884–1934, P. 24–33; *Chem. Abs.*, 1934, V. 28, Col. 5675.

An illustrated discussion touching upon the intramolecular transformation, the mol. structure of keratin and elastic properties. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 6313.) (W)

Animal Hairs: Constitution of. II. Chemical Interpretation. J. B. Speakman. *J. Soc. Dyers Col. Jubilee Issue* 1884–1934, P. 34–45.

S. deals with amino acid analysis and physicochem. research on the skeletal structure of the keratin mol. The chemistry of wool is regarded as the chemistry of long peptide chains, bridged across by disulfide, salt, and perhaps other linkages. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 6313.) (W)

Artificial Fibres: Use of Gelatin for the Production of. Fritz Ohl. *Gelatine, Leum, Klebstoffe*, 1934, V. 2, P. 99–102.

In spite of the com. importance of cellulose fibre, the search has not been abandoned for a method of producing fibre from a protein or a protein-like material. A suitable product resulted when a gelatin fibre was formed in a warm aq. soln. of $CaCl_2$ and drawn, under tension, through a coagulating bath. By the addn. of softening agents, like Turkey-red oil, the practical demands of extensibility can be met. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 7022.) (W)

Raw Wool: Detergent Action and the Deterioration of—When Washed with Sodium Carbonate, Soap or Gardinol. K. Schumann. *Textil-Forsch.*, 1934, V. 16, P. 43–5; *Chim. & Ind.*, V. 32, P. 415; *Monatschr. Textil-Ind.*, V. 49, P. 184.

Samples which had been washed under identical conditions were drained, dried at 70–2° and weighed to det. the loss on washing. The destructive action of the detergent on the raw wool can be estd. by detg. the amt. of

oxidizable matter in the wash waters. Kubel-Tieman's $KMnO_4$ method can be used with Na_2CO_3 and soap, and Froboese's Cl no. method with gardinol. Tests carried out on solns. of the reagents before and after washing, and at the same time on distd. H_2O, showed no appreciable differences under conditions similar to those prevailing in cm. practice, showing that the above reagents exert no injurious effect on wool. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 7031.) (W)

SILK FIBROIN: STUDIES ON THE PARTIAL HYDROLYSIS OF. Toyoo Uchino. *J. Biochem.* (Japan), 1934, V. 20, P. 65–130; *Chem. Abs.*, 1934, V. 28, Col. 6743. (W)

STATIC ELECTRICITY IN WORKING RAYON. H. Seifart. *Kunstseide*, 1934, V. 16, P. 307–12.

Two different methods of avoiding the disturbances due to the formation of electrostatic charges in the working of rayon, particularly acetate rayon, are discussed. The first method which involves preventing formation of the static electricity is to choose suitable surfaces with which the rayon comes into contact or incorporate materials into the filaments. The second method involves the use of devices for discharging the electrostatic charge. Various known examples of these methods are described. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 7026.) (W)

VISCOSE: DETERMINING OF RIPENESS AND THEORIES OF RIPENING OF (German). Dr. Heinrich Lotze. *Die Kunstseide*, 1934, V. 16, No. 9, P. 290–295.

Various methods for the determination of the degree of ripening and the theories of ripening are reviewed critically. The importance of ripening in practical manufacturing work is pointed out. Numerous references together with chemical equations and charts make the article of interest and importance as a reference. (S)

II. YARNS AND FABRICS

ELECTRICITY AND RAYON. (German.) H. Seifart. *Die Kunstseide*, 1934, Vol. 16, No. 9, P. 307–312.

In this article the formation of static electricity on the filaments is discussed. Following this different means are suggested for overcoming disturbances caused by static. Two principal groups are explained. In one it is attempted to prevent the formation of static electricity while in the other the electric charge once established is removed. Several types of devices which are already known are described in detail and finally the possibility of making profit from static electricity by using it to singe fabrics or yarns is noted. Japanese experiments on the insulating power of rayon are mentioned. (S)

ELONGATION VERSUS TENSION IN FINE DENIER VISCOSE RAYON YARNS. Herbert R. Mauersberger. *Rayon and Mell. Tex. Mo.*, August, 1934, P. 30–31, 32.

A brief article which omits any detail as to test method; gives data in the form of charts and tables on the variation in tension and stretch in rayon

yarns, both lustrous and delustered, as the relative humidity, tension, and the size or denier of the yarn are varied. It is stated, from one set of plots conducted at varying humidities from 60–75% relative to saturation, that the elastic limit of the yarns in each case occurring at less than 2% extension occurs at lower loads for higher humidities. On this basis it is recommended that humidities not in excess of 55% relative be employed. (Room temperature assumed to be at 70% F.) It is further shown that the denier of the yarn (at least for delustered yarns) has an effect on the location of the elastic limit, which again occurs at a point less than 2% extension, but at increasing tensions as the denier size of the yarn increases. All tests reported are for viscose type 100 denier 40 filament material. The tests carried out to show the variation of tension and elastic limit with denier were conducted at 60% relative humidity. (S)

INSECT DAMAGE TO RAYON MATERIALS. (German.) K. Langer and H. Bach. *Die Kunstseide*, 1934, V. 16, No. 11, P. 412–415.

This article indicates how ryaon may be attacked by insects. Excrements containing undigested particles of rayon have been found on several occasions. Photo-micrographs are given showing damaged goods and several instances of filaments showing an actual section bitten from the material itself. Most of the examples noted are in knit goods. (S)

PHOTOCHEMICAL DECOMPOSITION OF SILK. M. Harris. *B. S. J. Rsch.*, July, 1934, P. 151–5.

The purpose of this investigation was to study the deterioration of silk on exposure to daylight under natural conditions of use. The strength of silk cloth decreased and its ammonia nitrogen content increased on exposure to sunlight. Samples of the cloth treated with 1/10th normal solution of sodium hydroxide showed smaller changes and samples treated with 1/10th normal solution of sulfuric acid greater changes than the untreated cloth under the same conditions. Similar results were obtained on exposure of samples to north skylight. Samples treated with sodium carbonate solution of 1% or less in concentration showed the greatest stability. The amino nitrogen content was the same for silk stored in the dark and silk exposed to sunlight for three months. The rate of hydrolysis in 0.5 normal sodium hydroxide solution, measured by the formation of amino nitrogen, was the same for both samples. The decrease in breaking strength and increase in ammonia nitrogen content of silk on exposure to light are brought about by atmospheric oxidation in the presence of light. The results of these experiments are in accord with those obtained in the accelerated aging tests of silk, using the carbon arc lamp as a light source. (Copied complete from *Eastman Kodak Abs. Bull.*, Oct., 1934, P. 368.) (S)

WOOLEN AND SEMI-WOOLEN MATERIAL: RESULTS OBTAINED WITH ALCOHOL SULFONATES IN THE FELTING AND WASHING OF. Paul Hoff. *Z. ges. Textil-Ind.*, 1932, V. 35, P. 408.

Alcohol sulfonate renders the worsted textile smooth and soft after a short period of washing, protects the woolen fibres generally against excessive action of the alkali, and exerts a protective effect on sensitive dyes. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 7030.) (W)

WOOLEN AND SEMI-WOOLEN GOODS: WASHING OF DYED. B. Faden. *Monatschr. Textil-Ind.*, 1934, V. 49, P. 159.

Full directions are given for washing dyed woolen and semi-woolen goods. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 7030.) (W)

III. CHEMICAL AND OTHER PROCESSING (NOT OTHERWISE CLASSIFIED)

ADSORPTION OF EMULSION BY VISCOSE RAYON. K. Tanemura and K. Nishimura. *J. Soc. Chem. Ind. Japan* 37, Suppl. binding, 1934, P. 122–4.

The adsorption of olive oil or oleic acid emulsions by viscose rayon was studied; the pH of the emulsions was varied. The emulsifiers used were soap, Leonil LE (Höchst) and Nekal AEM (I. G.). Emulsions with soap as emulsifier were negatively charged, while those obtained with Leonil LE and with or without addn. of org. acid were positively charged. The adsorption of olive oil or oleic acid (Leonil LE or Nekal AEM as emulsifier) increased with decreasing pH; an optimum existed at pH 3.5. The positively charged olive oil or oleic acid particles were attracted and adsorbed on viscose rayon better than those negatively charged. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 4594.) (W)

ALPHA-CELLULOSE: DETERMINATION OF. C. Kilbourne Bump. *Ind. and Eng. Chem., Anal. Edition*, May 15, 1934, P. 223–25.

In a preliminary study of the effect of concentration of alkali on the tentative standard method proposed by the Division of Cellulose Chemistry of the American Chemical Society, determination of alpha-cellulose was made. In studying the effect of time on the treatment of cellulose with 17.5% sodium hydroxide the characteristic curve was found which showed rapid losses in weight of cellulose at first and soon approached a nearly constant value. A curve of the same type giving the same nearly constant value was found for 10% sodium hydroxide. A method for the determination of alpha-cellulose has been proposed temporarily which eliminates exact specifications of time and sample-reagent ratio. The suggested method has been tested on six commercial pulps. (S)

BLEACHING COTTON CELLULOSE WITH SOLUTIONS OF CALCIUM AND SODIUM HYPOCHLORITES: COMPARATIVE EXPERIMENTS ON. D. Halperin, D. Tumarkin and B. Kozlovskii. *J. Applied Chem.* (U. S. S. R.), 1933, V. 6, P. 536–45.

$Ca(OCl)_2$ solns. are distinguished from those of NaOCl having the same original content of active Cl by a higher "activity," *i.e.*, higher bleaching and oxidizing powers, the difference being particularly noticeable when NaOCl solns. are used with an excess of alkali. The consumption of the active Cl is in the following decreasing order: $Ca(OCl)_2$ soln., "neutral" soln. of NaOCl and "alk." soln. of NaOCl. The difference in the bleaching power of the solns. is particularly noticeable for low concns., disappearing for the high ones. The destructive power of the solns. in bleaching is evident only for severe conditions such as a temp of 30°. Since the effect of all the solns. is the same, preference should be given to the most economical. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 4221.) (W)

CELLITON FAST BLUE 3R. Georg Rudolph. *Kunstseide,* 1933, V. 15, P. 361.

A discussion of the use of this dye for discharging colors on acetate rayon and on acetate-viscose rayon mixts. It is the first blue dye of this class that will give white discharges. (Copied complete from *Chem. Abs.,* 1934, V. 28, Col. 4236.) (W)

DESIZING OF COTTON GOODS. Chas. E. Mullin. *Indian Textile J.,* 1934, V. 44, P. 205–7.

The removal of starch sizes from cotton goods by the acid steep and enzyme process with a consideration of the factors involved is discussed. (Copied complete from *Chem. Abs.,* 1934, V. 28, Col. 4603.) (W)

DYE ABSORPTION OF COTTON FIBRES: EFFECT OF GROWTH CONDITIONS ON THE. W. M. Mebane and A. A. O'Kelly. *Am. Dye. Rptr.,* July 16, 1934, P. 393–95, 418–20.

As a result of the test described it is noted that the growth condition determines the dyeing properties of cotton fibres. Further, that the differences in the dyeing properties of the various types are due to both physical and chemical differences in the fibres, and that cotton gathered under conditions most favorable to produce normal fibres gives the best results when dyed. The article is illustrated with rather poor photomicrographs of cotton fibre and several tables are given indicating the manner of dyeing the fibre and the results of these dyeings together with the dyes used. (S)

DYEING AND PRINTING INDUSTRIES: TENDENCIES IN THE. G. Martin. *Bull. soc. chim.,* 1933, V. 53, P. 1001–15; *Rev. gén. mat. color.,* 1934, V. 38, P. 169–77.

A description is given of the adjustment of processes to utilize and combine insol. azo and vat colors, which have different chem. properties, in order to obtain new color effects on materials made from cellulose fibres. (Copied complete from *Chem. Abs.,* 1934, V. 28, Col. 4235.) (W)

DYESTUFFS: STRUCTURE OF. J. T. Hewitt. *Sci. J. Roy. Coll. Soc.,* 1933, V. 3, P. 27–39.

A critical review of the types of org. compds. which produce absorption in the visible region of the spectrum, and the methods used in detg. types of linkage where different tautomeric structures are possible. (Copied complete from *Chem. Abs.,* 1934, V. 28, Col. 4235.) (W)

DYES OF THE BENZOPYRYLIUM TYPE: SPECTROGRAPHIC INVESTIGATION OF. II. FURTHEG OBSERVATIONS ON THE ABSORPTION SPECTRA OF FLAVYLIUM CHLORIDES. K. Hayashi. *Acta Phytochim.* (Japan), 1933, V. 7, P. 143–68; cf. *Chem. Abs.,* 1933, V. 27, P. 4677; 1934, V. 28, Col. 4235. (W)

RAYON YARNS AND FABRICS: NON-CREASING. H. Roche. *Silk J.,* 1933, V. 10, No. 112, P. 22–3; No. 113, P. 23–4.

Various methods of obtaining non-creasing rayon, either by altered mfg. processed or treatment of the yarn or fabric, including the use of rubber latex and the synthetic resins, are briefly discussed. (Copied complete from *Chem. Abs.,* 1934, V. 28, Col. 4241.) (W)

UNSHRINKABLE FINISH. A. T. King. *Chem. & Ind.*, 1934, P. 339–42.

A general discussion on the effect produced on wool by the new unshrinkable treatment. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 4603.) (W)

YARN AND TWIST NUMBER BY GRAPHICAL MEANS. (German.) C. Heinrich. *Die Kunstseide*, April, 1934, P. 140–43.

Twisted yarns of different materials are used frequently in modern textile practice and it often happens that the number of the plied yarn must be calculated. In this article a graphical method is shown which permits obtaining the number of the final yarn without calculation even in those cases where the yarns to be employed have different numbering systems, as, for instance, rayon and wool, etc. The chart also includes various methods of combination of different numbered yarns. (S)

WASTE WATERS IN DYE WORKS: CLARIFICATION OF. Arnold Rhode. *Deut. Färber-Ztg.*, 1933, V. 69, P. 333–4; *Dept. Sci. Ind. Research, Water Pollution Research, Summary Current Lit.*, V. 7, P. 102.

The concd. dye waste waters and strongly polluted rinsing waters are sepd. according to the type of dye, decolorized with HCl, CaO and chloride of lime in preliminary clarification tanks, and then treated with the remaining waste waters in two groups of 3-stage filters of brown-coal slag fitted with perforated clay pipes for better aeration. (Copied from *Chem. Abs.*, 1934, V. 28, Col. 4238.) (W)

WATERPROOFING RAYON YARNS AND FABRICS. H. Roche. *Silk J.*, 1934, V. 10, No. 115, P. 24–5, No. 117, P. 21, 34.

Rubber is applied to viscose and acetate materials by spraying and, after drying, is vulcanized. One method is by successive treatment with H_2S and SO_2, which liberates S. A gray fast to washing, light and rubbing can be obtained on acetate rayon by treating it for 45 min. at 75° in a 50 to 1 bath contg. a 10% aq. colloidal dispersion of graphite contg. 1 g. of NH_4CNS and 55 cc. of 30% rubber latex per l. Vermilion or Prussian blue can replace the graphite. Proofing and a dull finish are obtained by treating at 80° in a bath contg. 20 cc. of 30% rubber latex and 10 g. of ZnO per l. Ca phosphate, $BaSO_4$ or ZnS can also be used. Other methods are discussed of proofing with rubber soln. or latex, solns. or emulsions of waxes, metallic soaps, Al acetate and formate, etc. (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 4241.) (W)

IV. RESEARCH METHODS AND APPARATUS

ABSOLUTE VISCOSITY OF HIGH VISCOSITY SOLUTION: DETERMINATION OF THE. (German.) Dr. R. Focke. *Die Kunstseide*, May, 1934, P. 146–47.

A brief discussion including the mathematical formulae necessary to determine the viscosity of extremely viscous solutions by means of a capillary tube under controlled conditions. A closed vessel into which vapor or inert gas at known pressures is introduced is used to force the high viscosity liquid into a standard capillary tube against atmospheric pressure. The liquid which passes through the capillary is measured for volume in a standard measuring cell and the length of time necessary to carry out the

work is indicated. The whole instrument is immersed in a constant temperature bath. (S)

CINÉ PHOTO-MICROGRAPHY. Anon. *Brit. J. Phot.*, Feb. 23, 1934, P. 108.

A very brief discussion indicating how certain adjustments may be made to obtain a clean cut image in focus on the film. Note is made of the use of a vibrating device at the rate of 50 cycles per second for the ground-glass screen which had been oiled to give better light transmission and upon which the image of the microscopically studied specimen was projected. A moving picture camera in turn was focussed on this same ground-glass screen. The ground-glass was vibrated to overcome the effect of the grain. It is stated that using a 15 ampere carbon arc, condenser, heat-absorber, and thin ground-glass below the sub-stage condenser, successful pictures were made at normal speed in Koda-color. (S)

COLOR ANALYZER: NEW TYPE. Bausch and Lomb Optical Co. *Instr.*, 1934, V. 7, No. 8, P. 168.

The instrument provides a means of comparing the standard Munsell color disks having variable sectors of the different standard shades calibrated to read numerically for interpretation against a specimen of any type. This instrument differs from previous designs following the principle involved, however, in that a motor is provided to rotate a prism which in turn scans the disks. The disks, therefore, do not have to be rotated and can remain stationary for very simple adjustment. In operation the specimen is placed on one side and the Munsell disk on the other. The optical system provides means by which the two fields are brought into common adjacence so that they may be studied for match. The sectors on the Munsell disks are altered until a match is obtained and then the numerical scale accompanying the disk may be read and reference made to standard tables for the final set-up. It is also possible to insert a negative lens in the path of the light coming from the sample so that a larger field of view may be obtained whenever the sample is of uneven color. The field is approximately three times the size of that usually employed. (S)

HÖPPLER VISCOSIMETER. Dr. F. A. J. Zeidler. *Instr.*, 1934, V. 8, No. 7, P. 172.

A new instrument built in two styles, one for laboratory use of extraordinarily wide range and high precision, and the other for an industrial model which is intended primarily for convenience at low cost. The principle of operation is the eccentric descent of balls of various sizes in a closed column of liquid. It is stated that the instrument is especially suitable for the investigation of dark and opaque liquids and that all viscosities can be measured from the lightest petroleum ether to barely fluid tar at 20 degrees C. and at higher temperatures. It is said that the precision is plus or minus three quarters of one per cent. (S)

VISCOSITY: SOME SIMPLIFICATIONS IN THE PROCEDURE OF DETERMINING THE —OF CUPRAMMONIUM SOLUTIONS OF FIBRES. D. I. Tumarkin. *J. Applied Chem.* (U. S. S. R.), 1933, V. 6, P. 326–32.

The customary method for the detn. of the viscosity of the cuprammonium soln. was modified. The preliminary drying was either discarded

when air-dry samples were used or the samples were dried with alc. and ether and by heating for 30 min. at 96–100°. In the last case the wet fibre was pressed in a Büchner funnel and stirred in a porcelain dish with strong alc., the alc. was then removed, the operation repeated and the product treated finally a few times with ether. The operation can also be carried out with acetone. The substance was finally dried for 30 min. at 96–100°. In the viscosity detn. by dissolving the fibre in the Scheider soln. (Cu $1.3 \pm 0.02\%$, NH_4OH $15 \pm 0.2\%$, sugar 1%, the conen. of the fibre being 1%, *i.e.*, 1 g. in 100 cc. soln.), the soln. of the fibre was carried out in the app. and the metal ring used for agitation was replaced by Hg. The operation of the viscometer is described in detail. The exptl. results were quite satisfactory, a great saving in time being effected (only 3–7 hrs. was required for the entire operation). (Copied complete from *Chem. Abs.*, 1934, V. 28, Col. 4225.) (W)

WOOL: DETERMINATION OF SULPHUR AND SULPHATE IN. Ralph T. Mease. *B. S. J. Rsch.*, Nov., 1934, P. 617–23.

Sulphur is present in wool as an essential constituent of the wool substance, presumably in one constituent of the molecule, the amino acid, cystine. The amount varies with the type and quality of the wool and with the severity of processing. Thus cystine sulphur is of considerable practical significance. Sulphate sulphur is formed in wool through the action of light and other agencies on this sulphur and is acquired by wool from solutions used in carbonizing, dyeing or finishing. Therefore it is necessary to distinguish between the cystine sulphur of the wool and sulphate sulphur.

The total sulphur in wool is determined by completely oxidizing a specimen in an oxygen bomb, absorbing the oxidized sulphur in ammonium carbonate solution, precipitating and weighing it as barium sulphate. The sulphate sulphur is determined by dissolving a specimen of the wool in hydrochloric acid, precipitating and weighing the sulphate as before. Under the conditions recommended, the dissolved wool does not interfere and the cystine sulphur is not precipitated. The results reported indicate that with these methods either form of sulphur can be determined to within 2% of the amount present. (C)

V. ECONOMICS AND MISCELLANY

A SIMPLE METHOD FOR THE DETERMINING OF THE QUALIFICATION AND SKILL OF YOUNG WORKERS FOR THE TEXTILE INDUSTRY. (German). O. Bitzenhofer. *Die Kunstseide*, 1934, V. 16, No. 11, P. 415–419.

An article with a number of tables and much interesting material listing a series of tests together with the necessary equipment and suggestions for their carrying out of the work covering an examination accomplished by means of simple self-made tools and devices. Training time is said to be reduced to a minimum and training costs and loss by production of inferior quality goods can be largely avoided by proper selection of the worker according to his skill and aptitude for given types of work. (S)